AN EVALUATION OF THE ATTENUATION MECHANISMS
FOR DISSOLVED AROMATIC HYDROCARBONS FROM GASOLINE
SOURCES IN A SANDY SURFICIAL FLORIDA AQUIFER

By

JOSEPH TIMOTHY ANGLEY

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

AN EVALUATION OF THE ATTENUATION MECHANISMS
FOR DISSOLVED AROMATIC HYDROCARBONS FROM GASOLINE
SOURCES IN A SANDY SURFICIAL FLORIDA AQUIFER

by

JOSEPH TIMOTHY ANGLEY

December 1987

Gasoline is a significant source of groundwater
contamination in Florida. This results from the large
numbers of gasoline storage tanks, high rainfall, reliance
on groundwater-based potable water supplies and the
hydrogeology of Florida. Sorption, biodegradation and
hydrolysis of dissolved aromatic hydrocarbons (all isomers
of $C_6H_6-C_9H_{12}$) were determined in multicomponent experiments
with natural aquifer materials under saturated conditions.
Hydrogen peroxide, air, oxygen gas and ammonium chloride
treatments were evaluated as methods to enhance microbial
degradation of aromatic hydrocarbons. The solutes and
sorbents were from a gasoline contaminated aquifer in
central Florida. This site was typical of sandy surficial

xiii

aquifers in Florida with a low organic carbon content (0.015%). The aquifer was composed primarily of fine to medium grained sands.

Hydrolysis was not a significant removal mechanism for the selected aromatic solutes. Equilibrium batch isotherms and column studies determined sorption coefficients for aromatic solutes ranging between 0.045 and 0.1 with retardation values between 1.36 and 2.40. Column breakthrough curves exhibited minimal effects of adsorption non-equilibrium. Sorption isotherms were linear through the concentration range tested and no significant hysteresis was noted. Partitioning and surface dependent adsorption were evaluated by regression of column K_{oc} data with literature values of K_{ow}, water solubility and first order connectivity indices. No single model fully described the sorption process, and the sorption mechanism appeared to be a combination of several processes. Competitive solute interactions were not shown to be significant.

Column biodegradation experiments with acclimated microorganisms were performed at flow velocities close to those from the contaminated aquifer. Half lives ranged from 0.940 hr for benzene to 0.086 hr for n-propylbenzene at 0.680 cm/min. Branched aromatic solutes were more easily degraded in column studies.

Batch studies demonstrated the ability of field microbes to degrade aromatic hydrocarbons to less than 0.5 ug/L given sufficient oxygen. Microbes were not phosphorus

or nitrogen limited. Hydrogen peroxide increased dissolved oxygen, but did not lead to increased hydrocarbon removal in lab studies. Ammonium chloride produced nitrifying conditions. Oxygen augmentation with air and oxygen gas was shown to enhance biological removal of aromatic hydrocarbons.

Groundwater contamination is a topic of great scientific interest and public concern. Groundwater provides approximately 100 million people with potable water in the United States (Hoag and Marley, 1986) and nearly every state contains some number of contaminated wells (Barbash and Roberts, 1986). The sources of groundwater contamination are numerous. These include seepage from lagoons and impoundments, landfills, agricultural and silvicultural practices, accidental spills and leaking storage tanks and transfer equipment.

Gasoline and petroleum products are some of the most common groundwater pollutants. The potential magnitude of this problem is evident from the volume of petroleum used in the United States. Approximately 110 billion gallons of motor fuels are stored underground each year, in an estimated 1.4 million underground storage tanks, 85% of which are unprotected steel tanks with finite lifetimes (Hoag and Marley, 1986). It is expected that 10 to 30% of these tanks may leak (Dowd, 1984).

Gasoline contamination of groundwater in Florida is a particularly serious problem. This results from the confluence of three factors: the large number of petroleum storage tanks in the state, the reliance on groundwater

based potable water supplies, and the hydrogeology of Florida.

The major sources of petroleum contamination in Florida are leaking storage tanks and pipes. The high water table in the state leads to conditions favorable for corrosion. As of February 1986 there were 455 known storage tank incidents resulting in 368 cases of groundwater contamination. The total volume of spilled gasoline exceeds 4.2 million gallons (FLDER, 1986). The remaining 60,000 petroleum storage tanks in the state provide potential sources for future groundwater pollution.

These sources of contamination are particularly significant owing to the importance of groundwater in Florida. Groundwater withdrawal for potable water use is approximately 1400 Mgal/d, comprising 87% of public water and 94% of rural water supplies. It is noteworthy that nearly 2 million residents drink untreated water from shallow private wells which are particularly prone to contamination from underground storage tanks (Fernald and Patton, 1984).

Hydrogeology is the third factor which contributes to the sensitivity of Florida's water supplies to gasoline contamination. Most of the potable water aquifers are surficial or intermediate in depth, and are susceptible to contamination. In addition, the generally porous nature of top soil in the state enhances pollutant transport to the underlying aquifers. Most soils in Florida are sandy loam,

sandy clay and sandy clay loams, all of which are noted for their relatively high permeabilities (Fernald and Patton, 1984). The sandy deposits of the Pliocene and Pleistocene ages common to Florida are also marked by low organic carbon and clay content (Fetter, 1980), resulting in high permeability and low sorptive capacity.

Given the magnitude of this problem, the transport and environmental reactions of dissolved gasoline components in shallow sandy aquifers is an important area of study. This is particularly true of the aromatic constituents of gasoline, owing to their toxicity, concentrations in gasoline and their high aqueous solubility. Gasoline products which are released into the vadose zone travel downward under the influence of capillary and gravitational forces. When the sorptive capacity of the soil is exceeded, gasoline moves onto the groundwater table, where it spreads laterally across the top of the saturated zone. This is a result of the density of gasoline ($0.7-0.75$ g/cm^3). Gasoline components partition into the water to the extent of their water solubility, and move in the direction of the water table gradient.

Physical, chemical and biological factors must all be considered in the determination of the fate and transport of dissolved gasoline hydrocarbons in groundwater. The interaction of these factors may be conveniently examined in the context of a generalized mass transport equation. A one-dimensional form of this equation is

$$\partial C/\partial t = D_h (\partial C/\partial x^2) - v(\partial C/\partial x) - p/\theta(\partial S/\partial t) - Q_i \quad [1.1]$$

where C = solution phase concentration of solute (ug/L)
S = adsorbed phase concentration of solute (ng/g)
θ = volumetric water content (mL/cm^3)
t = time (min)
x = horizontal distance (cm)
p = bulk density (g/cm^3)
D_h = hydrodynamic dispersion coefficient (cm^2/min)
v = average pore water velocity (cm/min)
Q_i = degradation rate (min^{-1})

The components of this equation are convection, dispersion, sorption and degradation terms. Convection describes the movement of a dissolved contaminant with the groundwater. Dispersion describes the spreading of the solutes during flow through the aquifer material. Sorption terms account for the retardation of the dissolved solutes by interaction with the aquifer matrix, and degradation terms evaluate the removal or transformation of the contaminants. Research has shown that sorption and biological degradation are the major attenuation mechanisms for organic solutes in soils and groundwater (Woodburn, 1985).

Mathematical models based on such equations are important tools for the prediction of contaminant movement (Pinder, 1984). However, the adequacy of these predictions is directly related to a knowledgeable and accurate quantification of the processes involved (MacKay et al., 1985). The remediation of groundwater contamination also

requires detailed and usually site specific data for these processes.

This dissertation presents a detailed investigation of the attenuation of selected dissolved aromatic gasoline hydrocarbons in a typical sandy surficial aquifer in Florida, using a variety of batch and column techniques. Sorption coefficients and biological and abiotic degradation rates from laboratory studies are presented. These studies simulated conditions at a contaminated field site and included experiments to assess various treatment alternatives. Actual field data are summarized, and compared to the laboratory data.

The improved understanding obtained from the collection and analysis of these data should aid in the formation and improved use of predictive models describing the movement and reaction rates of water soluble components of gasoline in shallow groundwater systems and aid in the selection of appropriate groundwater reclamation technologies.

CHAPTER II
OBJECTIVES

The main objectives of this study were:

(1) To evaluate the sorption coefficients for 12 selected aromatic hydrocarbons found in water at the Lake Alfred research site, employing batch isotherms and soil columns;

(2) To determine the rates of hydrolysis of the 12 selected aromatic hydrocarbons;

(3) To determine the rates of biodegradation of the 12 selected aromatic hydrocarbons under simulated field conditions, and after treatment with hydrogen peroxide, oxygen gas and ammonium chloride;

(4) To determine the most appropriate predictive model for sorption of the 12 selected aromatic hydrocarbons in a sandy surficial aquifer in Florida;

(5) To correlate molecular properties of the selected aromatic hydrocarbons with sorptive and biological parameters;

(6) To evaluate field data based on the laboratory measurements of sorption and biodegradation and

(7) To extrapolate the laboratory data for application of aquifer remediation practices.

CHAPTER III
LITERATURE REVIEW

3.1 Introduction

This chapter presents a review of the pertinent
literature for the reactions of gasoline derived aromatic
hydrocarbons in groundwater. The major areas of discussion
are the environmental effects of gasoline contamination, the
use of advection-dispersion transport models, the sorption
of aromatic compounds to aquifer materials, and the
biodegradation of aromatic compounds in groundwater systems.

3.2 Environmental Effects of Gasoline Contamination

Gasoline is a complex mixture of many hydrocarbon
compounds. A typical gasoline contains between 150-250
identifiable hydrocarbon components (Sanders and Maynard,
1968) consisting of alkane, alkene, aromatic and napthene
hydrocarbons. Automobile gasolines are comprised of C_5-C_{12}
hydrocarbons with boiling points in the range 32-210 C. Un-
leaded gasolines contain greater concentrations of aromatic
hydrocarbons to provide for anti-knock protection and
branched hydrocarbons to increase octane ratings (Moore and
Moore, 1976).

Despite the large number of hydrocarbons comprising gasoline, much of the environmental concern focuses on the water soluble components of gasoline, particularly the single ring aromatic compounds. These compounds are of concern based on their toxicity, aqueous solubility and concentration in gasoline (Barker and Patrick, 1985). Acute toxicity is associated with the water soluble fraction of oils (Blumer et al., 1973) and the major components of the water soluble fraction are aromatic (Coleman et al., 1984). Data from the work of Coleman et al. (1984) showed that although aromatic components made up only 50% of the unleaded gasoline product in their study, 87-95% of the components in the water soluble fraction were aromatic. Thus in a spill situation a significant amount of the contaminants in the water phase will be aromatic. Selected physical properties of the compounds used in this study are listed in Table 3-1.

The health effects from the use of gasoline contaminated water may be significant. Benzene is a carcinogen in rats and mice and exposure is linked with leukemia (USPHS, 1981). The maximum contaminant level for benzene in community drinking water supplies is 1 ppb in Florida. Toluene, ethylbenzene and m-xylene affect the central nervous system (Windholtz, 1976). Unleaded gasoline induces renal and hepatocellular carcinomas in rats and the use of petroleum contaminated water can produce elevated levels of indoor air pollutants allowing chronic exposure to

Table 3-1. Selected physical properties of study compounds.

Compound	Molecular[a] Weight, AMU	Water[b] Solubility, mg/L	Boiling[a] Point, °C	Density,[a] g/ml	log[c] K_{ow}	$_1\chi$[d]
Benzene	78.11	1740–1791	80.1	0.8675	1.56–2.28	3.000
Toluene	92.13	515– 724	110.6	0.8669	2.11–2.73	3.394
Ethylbenzene	106.2	131– 208	136.2	0.8670	3.15	3.932
m,p-Xylene	106.7	134– 196	139.1	0.8642	3.18	3.788
			138.4	0.8611		
o-Xylene	106.7	142– 213	144.4	0.8802	2.77–3.13	3.805
3,4-Ethyltoluene	120.2	40	161.3	0.8645		4.326
			162.5	0.8616		
1,3,5-Trimethylbenzene	120.2	48– 92	164.7	0.8652	3.42–3.60	4.182
2-Ethyltoluene	120.2	40	165.2	0.8807		4.343
1,2,4-Trimethylbenzene	120.2	52– 59	169.3	0.8758		4.198
1,2,3-Trimethylbenzene	120.2	75	176.1	0.8944	3.60	4.215
Isopropylbenzene	120.2	48– 73	165.4	0.9106	3.60	4.305
n-Propylbenzene	120.2	55	159.2	0.8620	3.57–3.68	4.432

[a]CRC Handbook of Chemistry and Physics, 1980.

[b]Brookman et al., 1985.

[c]Leo et al., 1971.

[d]Sabljic, 1987.

hydrocarbons (Shehata, 1985). Dermal absorption of volatile organic contaminants from gasoline may also be a significant exposure (Brown et al., 1984).

Fire and explosion hazards are also a risk factor in the release of gasoline to the environment. Volatilization and subsequent gas phase transport of hydrocarbons in the unsaturated zone have destroyed buildings (Hoag and Marley, 1986).

3.3 Convective-Dispersive Models

The cogent evaluation of contaminant plumes, remedial action alternatives, and risk assessment for organic compounds in groundwater requires a thorough understanding of the behavior of these contaminants in groundwater systems. This includes an assessment and quantification of the relevant processes which influence their fate and transport (Miller and Weber, 1984).

The interaction of these processes may be examined in the context of convective-dispersive models. These models have been reviewed (Anderson, 1979, Freeze and Cherry, 1979) and are marked by their computational simplicity, reasonable data requirements and sufficiently accurate output (Roberts et al., 1985). Although the adequacy of convective-dispersive models for describing solute transport has been questioned (Anderson, 1979, Smith and Schwartz, 1980), particularly with regard to dispersivity

approximations, these models provide a convenient framework for understanding the transport of dissolved solutes in groundwater.

The general form of the solute transport equation under saturated flow conditions is given by Bear (1979). A one-dimensional form of this equation for conservative contaminants under steady flow conditions is

$$\partial C / \partial t = D_h (\partial^2 C / \partial x^2) - v (\partial C / \partial x) \qquad [3.1]$$

where
C = solution phase concentration of solute (ug/L)
S = sorbed phase concentration of solute (ng/g)
D_h = hydrodynamic dispersion coefficient (cm^2/min)
t = time (min)
x = horizontal distance (cm)
v = average pore water velocity (cm/min)

The major components of this equation are convection (bulk flow) and dispersion (deviation from bulk flow). A brief discussion of dispersion follows, with reference to extrapolation of laboratory data to field scale applications.

The hydrodynamic dispersion coefficient describes the spreading of a solute as it moves through porous media. Hydrodynamic dispersion (D_h) is the sum of mechanical dispersion, caused by differences in water velocity through sinuous and tortuous pores, and molecular diffusion (Biggar and Nielsen, 1962). Dispersion values reflect the heterogeneity of the aquifer material. Dispersion is usually determined by measuring the breakthrough of a conservative tracer such as chloride or tritiated water.

The physical and mathematical relationships of water and solute transport were reviewed by Davidson et al. (1983). Solute dispersion was noted to occur because of macroscale spatial changes in the direction and magnitude of water flow. The continuum approach to mathematically describe water and solute transport in laboratory soil columns was shown to be reasonably successful.

In practice, laboratory measurements and theory may be of little value in predicting dispersion in natural aquifers. Laboratory columns give dispersivity estimates on the order of centimeters, whereas field scale dispersion is usually in meters (Bedient et al., 1985). This is a result of the greater heterogeneity of a field site versus a small homogeneous laboratory column. A solution for equation [3.1] for a finite column using dimensionless variables was presented by Brenner (1962). The dimensionless Peclet number (P_e) was used as a measure of dispersion:

$$P_e = vL/4D_h \qquad [3.2]$$

where v is pore water velocity (cm/min), L is the length (cm) of the soil column and D_h is the hydrodynamic dispersion coefficient (cm^2/min). For values of $P_e > 100$ dispersion is assumed negligible. Values of $P_e < 10$ generally indicate complete mixing. Boundary conditions for displacement experiments through short laboratory columns were reviewed by van Genuchten and Parker (1984). The solution of Brenner (1962) was shown to correctly conserve mass in finite laboratory soil columns, based on mass

balance considerations. For a flux type inlet boundary condition (flowing concentrations), Brenner's solution was applicable provided the column Peclet number was not much less than five. The solution of Lapidus and Amundson (1952) was recommended to evaluate flux averaged concentrations in finite laboratory columns or semi infinite field profiles.

3.4 Sorption of Aromatic Compounds

Sorption is a major mechanism in the attenuation of organic solutes in the saturated zone. Solutes differentially sorb onto aquifer materials and thus are retarded in their movement through the subsurface, resulting in a chromatographic like separation of the soluble constituents of a plume, with groundwater as the mobile phase.

Sorption describes the transfer of solutes from a liquid phase to a solid phase (Miller and Weber, 1984). In this literature review the liquid phase is assumed to be water, containing solubilized organic solutes and the solid phase is the aquifer material under saturated, steady flow conditions. Sorption is influenced by the physical and chemical characteristics of the aquifer (ie., soil type, fraction of organic carbon), and the solute (ie., solubility, volatility, density).

Although sorption is a major component in the attenuation of solutes in the subsurface, the fundamental

processes of solute-soil interaction and the thermodynamics of this process are not completely characterized. Therefore, sorption is used in this study as a generic term to describe solute retention (ie. uptake of solute), regardless of whether the process is one of adsorption, absorption or partitioning (Woodburn, 1985). Desorption is used here to describe solute removal from the solid phase.

3.4.1 Sorption Processes

The attractive forces acting to effect sorption of hydrophobic compounds onto natural sorbents were reviewed by Voice and Weber (1983). The major theory is discussed below.

Bonding forces in sorption may be both physical and chemical, though both are basically electrostatic in nature. Physical sorption results from Van der Waals forces. The strength of these interactions is generally on the order of 1-2 Kcal/mole. These energies may be augmented by a thermodynamic gradient driving hydrophobic molecules out of solution. This is based on entropic considerations (solvophobic theory).

Chemical sorption is the interaction between specific sites of the sorbent and individual solute molecules. This approximates a true chemical bond with heats of adsorption between 15-50 Kcal/mole. Voice and Weber (1983) point out that it is difficult to assess the importance of each type of bonding. The heterogeneous nature of natural sorbent materials is largely unknown, and sorption processes probably involve all types of interactions.

3.4.2 Sorption Equilibria

Two experimental techniques are widely used to evaluate the $\partial S / \partial t$ term in equation [1.1]. These are batch equilibrium and soil column methods. Batch studies allow the evaluation of the linearity of the sorption isotherm and their use is well documented (Schwarzenbach and Westall, 1981, Chiou et al., 1979). The most widely used models to describe sorption equilibria in groundwater systems are the linear [3.3] and Freundlich models [3.4] (Miller and Weber, 1984):

$$S = K_d * C \qquad\qquad [3.3]$$
$$S = K_f * C^n \qquad (n < 1) \qquad [3.4]$$

where S (ug/g) and C (ug/L) are the adsorbed phase and solution phase concentrations respectively at equilibrium, K_d (L/g) is the linear sorption coefficient, K_f (L/g) is the Freundlich sorption coefficient (both K_d and K_f indicating sorption capacity) and n is an empirical constant (indicating sorption intensity). The linear model is in effect, a special case of the Freundlich model where n=1. The Freundlich equation is often linearized (log transformed) to facilitate calculation of variables K_f and n in batch studies:

$$\log S = n * \log C + \log K_f \qquad [3.5]$$

In column studies K_d is evaluated through the retardation factor (R). The mass transport equation for reactive solutes under steady flow is described by equation [3.6]:

$$\partial C/\partial t + p/\theta\, \partial S/\partial t = D_h\, \partial^2 C/\partial x^2 - v\, \partial C/\partial x \qquad [3.6]$$

where p is the bulk density, θ is the volumetric water content and S is the sorbed phase concentration. Note that equation [3.6] is equivalent to equation [3.1] with the addition of the sorption term $\partial S/\partial t$. Assuming linear, reversible sorption, the sorbed concentration of a solute is related to the aqueous concentration of the solute by the relationship:

$$\partial S/\partial t = K_d\, \partial C/\partial t \qquad [3.7]$$

Substitution for $\partial S/\partial t$ in equation [3.6] with equation [3.7] yields the relationship:

$$\partial C/\partial t + K_d\, \partial C/\partial t\, (p/\theta) = D_h\, \partial^2 C/\partial x^2 - v\, \partial C/\partial x \qquad [3.8]$$

After separation of variables equation [3.8] becomes

$$\partial C/\partial t\, [\,1 + p\, K_d/\theta\,] = D_h\, \partial^2 C/\partial x^2 - v\, \partial C/\partial x \qquad [3.9]$$

and by defining the retardation factor (R) as

$$R = 1 + p\, K_d/\theta \qquad [3.10]$$

substitution of equation [3.10] into [3.9] results in the incorporation of the retardation factor (R) into the mass transport equation for solute transport under saturated steady flow conditions:

$$R\, \partial C/\partial t = D_h\, \partial^2 C/\partial x^2 - v\, \partial C/\partial x \qquad [3.11]$$

Analysis of equation [3.10] indicates that the value of R is largely dependent on K_d for a homogeneous aquifer system or laboratory column. Determination of R from soil

column studies leads to the evaluation of K_d from equation [3.10]. Nkedi-Kizza et al. (1987) compared techniques for the calculation of R from soil column leaching experiments and from batch isotherm experiments. Values of R calculated by determining the area above the breakthrough curve were shown to be equivalent to R values calculated by using equation [3.10].

3.4.3 Sorption Estimators

Recently, approximation methods based on the assumption of partitioning as the dominant method of solute interaction have become common (Karickhoff et al., 1979, Chiou et al., 1979, Kenaga and Goring, 1980, Chiou et al., 1983). Their use is largely a result of the time and difficulty in the accurate measurement of sorption coefficients (K_d), and the general lack of data on hydrocarbon sorption to environmental sorbents. These authors note a correlation between the fractional organic carbon content of the sorbent material (f_{oc}) and K_d. The K_d normalized to f_{oc} of the sorbent is described as K_{oc} where:

$$K_{oc} = K_d/f_{oc} \qquad [3.12]$$

Values of K_{oc} is well correlated with aqueous solubility (WS) (Chiou et al., 1979) and the octanol-water partition coefficient (K_{ow}) (Karickhoff et al., 1979). These authors suggest that the solute-sorbent interaction is a partitioning process rather than an interaction between solute and the mineral surface. Evidence for partitioning is partially supported by the hydrophobic character of soil

organic matter, and by solvophobic theory (Rao et al., 1985). The general relationship between K_{oc} and K_{ow} and WS takes the form (Curtis et al., 1986):

$$\text{Log } K_{oc} = a * \text{Log } K_{ow} + \text{Log } f_{oc} + b \qquad [3.13]$$

$$\text{Log } K_{oc} = c * \text{Log WS} + \text{Log } f_{oc} + d \qquad [3.14]$$

where a,b,c, and d result from regression analysis of laboratory isotherm data and depend on the solute-sorbent system.

However, there are significant limitations on the use of these estimators, and the basis of partitioning as a sorption mechanism is questionable (Milgelgrin and Gerstl, 1983). In a strict sense, these relationships hold only for those compounds and sorbents used in the original studies (i.e., these are empirical relationships). This is reflected in orders of magnitude variation in estimates of sorption using these relationships. Application of the partitioning models may not be appropriate in experimental systems with solutes and sorbents which are different from those used to develop these models. In addition, these equations may not apply at organic carbon fractions less than 0.1% (Curtis et al., 1986). Rao and Jessup (1983) noted that the use of K_{oc} to estimate sorption can lead to significant errors with soils with very low (less than 0.1%) organic carbon contents.

Milgelgrin and Gerstl (1983) reviewed the evidence for partitioning and noted that a correlation between the organic carbon content of the soil and sorption was not

universally significant. These authors cited several studies where removal of organic carbon from a soil actually increased the amount of sorption, or had no negative effect on the sorption values. These authors suggested that molecular structure of the solute may be a better predictor of sorption to sediments than water solubility or octanol/water partition coefficients. This results from the observation that with a relatively rigid adsorbing surface, the conformation of the solute molecule will greatly affect its adsorption (i.e., steric effects), but not its partitioning between an organic phase and water.

Recently, first order molecular connectivity indexes (^1X) were shown to be well correlated with K_{oc} values (Sabljic, 1984, Sabljic, 1987). Molecular connectivity is described as a quantitative measure of the area occupied by the projection of the non-hydrogen skeleton of a molecule. The correlation between K_{oc} and the first order molecular connectivity index supports the contention that the process of soil sorption may be viewed as an attractive interaction between two planes, with the magnitude of the interaction directly proportional to the surface area of the molecule. This suggests that the soil sorption and partitioning process reflect different mechanisms. An accurate model of sorption may include both partitioning and surface area dependent affects.

The relationship between K_{oc} and ^1X is (Sabljic, 1987):

$$\text{Log } K_{oc} = 0.53 * {}^{1}X + 0.54 \qquad [3.15]$$

This relationship is based on literature values of K_{oc} from laboratory experiments with 72 compounds covering a broad range of polarities and classes, and a variety of sorbent systems. The correlation coefficient is 0.976 which explains 95.2% of the variance.

3.4.4 Desorption

In most cases sorption is considered to be completely reversible, that is, the adsorption-desorption isotherms are reversible and single valued. However, several investigators report desorptions which display hysteresis in batch studies (Bailey and White, 1970, Boucher and Lee, 1972, Carringer et al., 1975, DiToro and Horzempa, 1982). Van Genuchten et al. (1974) found that the exponent for desorption is concentration dependent, and described the hysteretic behavior by using separate isotherm equations for sorption and desorption:

$$S_{s} = K_{ds} \, C_{s}^{\ ns} \qquad [3.16]$$
$$S_{d} = K_{dd} \, C_{d}^{\ nd} \qquad [3.17]$$

where subscripts s and d indicate sorption and desorption respectively. Hysteresis in column studies was noted by Schwarzenbach and Westall (1981), although the reaction was termed reversible, since all the solute was eventually eluted from the column.

3.4.5 Sorption Kinetics

Hysteretical behavior may actually be a manifestation of sorption-desorption kinetics. Rao and Jessup (1983) noted that the influence of non-singular isotherms (ie., isotherms which display hysteresis) on solute movement may be less significant than the effects of sorption nonequilibria. In a study of the transport of pesticides at high concentrations, Rao and Davidson (1979) noted that the position of an adsorbed solute in a breakthrough curve was governed by the nature of the equilibrium adsorption isotherm equation, whereas the shape of the curve was defined by the kinetics of the sorption-desorption process.

Sorption reactions between hydrophobic pollutants and sediments are generally rapid and not rate limited (Weber et al., 1983). Rao and Davidson (1980) concluded that many sorption reactions are complete within one minute in batch slurry experiments, although longer times to equilibrium were noted in several studies (Karickhoff et al., 1979, Miller and Weber, 1984). Schwarzenbach and Westall (1981), in a comparison of solute breakthrough at various flow velocities, concluded that K_d values from column experiments where velocity was less than 10^{-3} cm/second were similar to K_d values from 18 hour equilibrium batch studies.

3.4.6 Aromatic Sorption Values From The Literature

There are few data in the literature addressing sorption of dissolved gasoline components in the subsurface. Much of the research involved aromatic compounds in single

solute experiments, simple mixtures, or data from crude oil studies.

Houzim (1978) observed a decrease in sorption in the order alkenes > aromatics > cycloalkanes > alkanes. Nathawani and Phillips (1977) in a study of hexadecane, o-xylene, toluene and benzene in crude oil on soils of varying organic matter presented sorption coefficients based on Freundlich isotherms. Rodgers et al. (1980) reported the adsorption and desorption of benzene on several soils and clays at 25 C. The aqueous phase concentration range was 10 to 1000 ug/L. Sorption of benzene was minimal, except on aluminum saturated clay. These data are summarized in Table 3-2.

Wilson et al. (1981) evaluated the sorption of toluene on a fine sand in a column study. A retardation factor less than 2 for the concentration range of 200-900 ug/L was reported. This indicates the relatively low retardation potential of sandy aquifers. The retardation factor describes the extent of solute transport relative to water. The retardation factor for water is defined as unity. Solutes with large retardation factors are less mobile and and their movement is retarded, relative to that of water.

Schwarzenbach and Westall (1981) presented data for the sorption of several chlorinated and alkyl benzenes on twelve natural aquifer materials with varying amounts of organic carbon. The initial concentrations of the alkylbenzene components were 20 ug/L. Sorption coefficients from batch

Table 3-2. Summary of adsorption data for aromatic hydrocarbons.

Soil	Percent Organic Content	Benzene		Toluene		o-Xylene	
		1/n	K	1/n	K	1/n	K
Silty Clay	16.2	1.272	3.23	1.008	3.52	0.947	11.03
Sandy Loam	10.8	1.298	0.583	1.002	2.69	0.707	4.77
Silty Clay	1.7	1.366	0.003	0.996	0.931	1.098	0.62
Silt Loam	1.0	1.51	0.028				
Silty Clay Loam	2.6	0.89	2.4				
Silty Clay Loam	1.8	0.94	1.8				
Al saturated Montmorillonite	0	1.08	30.9				
Cu saturated Montmorillonite	0	0.99	4.4				

Adapted from Brookman et al., 1985.

studies of a soil with low organic carbon (0.0015 g_{oc}/g soil) are shown in Table 3-3.

As may be noted from this short review, most of the above studies involve data from individual components or from oil based products. Given the differences in composition among these petroleum products and gasoline, extrapolation may be insufficient to provide accurate data (Brookman et al., 1985).

3.5 Biodegradation of Aromatic Hydrocarbons in Groundwater

Biological activity is an important process in the attenuation of gasoline hydrocarbons in the subsurface environment. This realization is only recent. Early techniques for the enumeration of microbes in the subsurface (Waksman, 1916) underrepresented the numbers of microbes in the subsurface, showing a decline in population with depth. These data resulted from the use of nutrient rich growth media, inappropriate for the enumeration of groundwater bacteria (Wilson and McNabb, 1983).

Recent work shows that more substantial populations of heterotrophic organisms exist in shallow water table aquifers than were previously thought. Wilson et al. (1983a) demonstrated that the numbers of organisms were relatively constant to a depth of six meters in a shallow water table aquifer. The populations of heterotrophic bacteria were estimated to be approximately 10^6 organisms/gram dry weight soil (Ghiorse and Balkwill, 1985).

Table 3-3. Sorption coefficients of selected aromatic
hydrocarbons on low organic carbon soil.

Compound	K_d	
	average	standard deviation
Toluene	0.37	0.12
p-Xylene	0.50	0.10
1,3,5-Trimethylbenzene	1.00	0.16
1,2,3-Trimethylbenzene	0.95	0.11

Source: Schwarzenbach and Westall, 1981.

A review of the techniques for the enumeration and estimation of microbial biomass were presented by Atlas (1982) and Webster et al. (1985). Bouwer and McCarty (1884) noted that the majority of bacterial activity was associated with bacteria attached to surfaces. This results in the formation of biofilms, which are favored in low substrate-high surface area conditions. The biofilm may also present an active surface with solutes sorbing to the surfaces of microbial cells. In terms of the advection-dispersion models, the rates of biological degradation are incorporated into the model through the sink term Q_i, which describes the microbial degradation of solutes from the aqueous phase. Q_i is defined as:

$$Q_i = -k \, \theta \, C \qquad [3.18]$$

where k is the rate of biological degradation (T^{-1}), θ is the volumetric water content (ml/cm^3) and C is the solution phase concentration of a solute (ug/L).

3.5.1 Environmental Factors Affecting Biodegradation

Many factors can affect the transformation of organic contaminants in the subsurface. McCarty (1984) included low substrate concentrations, toxic conditions, molecular structure of the substrate, inaccessibility of the substrate, and absence of essential growth factors Biological activity is often limited by certain metabolic requirements of the cell, supplied from the environment. Important geochemical properties include pH, redox potential, nitrogen and phosphorus concentrations and the

availability of an appropriate electron acceptor. Oxygen is used as the ultimate electron acceptor for aerobic degradation processes and is often a limiting factor in the degradation of hydrocarbons. Molecular oxygen is also essential to the aerobic metabolism of aromatic compounds, because it is incorporated into the structure of the metabolic products (Evans, 1977). The biochemistry of the aerobic metabolism of aromatic compounds is well established (Dagley, 1975). The first step in this metabolic pathway is the removal of side chains, followed by the enzyme (oxygenases) mediated hydroxylation of the aromatic ring. Assuming 50% conversion of carbon to biomass and incomplete oxidation of the hydrocarbon molecules, two parts of oxygen are required for the degradation of each part hydrocarbon (Wilson et al., 1986). The complete oxidation of hydrocarbon molecules to CO_2 and H_2O may require three to four parts of oxygen per part hydrocarbon.

There is some evidence for the anaerobic biodegradation of aromatic compounds in the environment. In the absence of oxygen, nitrates, sulfates and CO_2 become electron acceptors. Bouwer and McCarty (1984) presented a review of these processes. Nitrate respiration (Psuedomonas and Moraxella sp.) and methanogenic fermentation processes can reduce the benzene nucleus followed by hydrolysis to yield aliphatic acids (Evans, 1977). Wilson and Rees (1985) showed the anaerobic degradation of benzene, toluene, xylenes and alkylbenzenes under methanogenic conditions.

Over a six week period only toluene showed substantial degradation, but after 40 weeks, benzene was reduced by 72%, toluene by 99%, ethylbenzene by 74% and o-xylene by 78%. Nutrient addition decreased the rate of hydrocarbon removal. The metabolic products from the anaerobic degradation of the aromatic molecules were not investigated. Nitrate respiration of xylene in a river alluvium was demonstrated by Kuhn et al. (1985). However, anaerobic biotransformations occur extremely slowly (months), relative to aerobic processes which may be completed in a matter of hours (Wilson, 1985).

Physical properties of the aquifer also play an important role in determining the extent of microbial degradation. Porosity and hydraulic conductivity are significant parameters since the resupply of oxygen, substrate and nutrients to the microbial cells must come via the groundwater.

The concentration of the contaminant substrates is an important factor in the extent of biodegradation. High concentrations may result in incomplete degradation resulting from rapid depletion of oxygen and high substrate concentrations may also lead to increased acclimation times. Jensen et al. (1985) demonstrated an increase in the time required for acclimation (lag time) of bacterial cultures with increasing concentrations of napthelene. Lag times prior to substantial microbial degradation of a solute or nutrient reflects the time required by the indigenous

microflora to adapt to the added substance. Adaption is a phenomenon rather than a mechanism or process, and the term refers to an increase in the rate of biotransformation of a substance resulting from exposure to that substance (Wilson et al., 1983b). Low solute concentrations may result in the occurrence of a threshold limit, below which the microflora are unable to utilize the solute with out a cosolute (Wilson and McNabb, 1983). Jensen et al. (1985) demonstrated the degradation of aromatic molecules to less than 1 ug/L, implying that there was a very low threshold limit for the aromatic hydrocarbons. The relationship between concentration and biodegradation was reviewed by Alexander (1985). He stressed the importance of studying contaminant levels that exist in the environment.

3.5.2 Aromatic Biodegradation Values From the Literature

McKee et al. (1972) reported the oxidation of gasoline by Pseudomonas and Arthrobacter under aerobic but not anaerobic conditions. Degradation of gasoline by Pseudomonas was reported by Williams and Wilder (1971), and Litchfield and Clark (1973) showed significant numbers (10^4 cells/mL) of hydrocarbon degrading bacteria in groundwater contaminated with petroleum hydrocarbons from twelve sites. Bacterial populations appeared to be related to the concentrations of hydrocarbons. These data indicate the adaptation of microbial communities to the changing nutrient source (i.e., gasoline). The two major mechanisms of adaptation are induction of metabolic pathways, or the

activation or transfer of plasmids (Litchfield, 1986). This ability of microorganisms to adapt to the presence of contaminants forms the basis of in-situ biodegradation.

Several researchers have reported the biodegradation of aromatic compounds in groundwater. One shortcoming of most of this research is the lack of degradation rate coefficient data, required for use in groundwater transport models, and insufficient data on solute concentrations.

Jamison et al. (1976) reported the use of benzene as a sole carbon source. No rate coefficient data were given. McKenna and Heath (1976) noted the slow oxidation of benzene by P. putida. Delfino and Miles (1985) showed the degradation of benzene in 16 days under aerobic conditions in Floridan groundwater with an eight day lag phase. Ethylbenzene was degraded as a sole carbon source (Gibson and Yeh, 1973), but no rate data were given. Schwarzenbach et al. (1983) found toluene rapidly degrades within several meters in a study of river water infiltration to groundwater but rate and initial concentration data were not specified.

Kappeler and Wuhrmann (1978b) in a study of gas oil degradation reported that nitrogen and oxygen were the limiting factors in hydrocarbon degradation. Addition of NH_4Cl resulted in further microbial degradation, and cell densities were on the order of 10^6/mL. Lag times of 5-6 days were noted in the batch experiments. Kappeler and Wuhrmann (1978a) showed that microbes from uncontaminated groundwater can attack gas oil components. Lag times of 1

day at 25 C and 5 days at 10 C were reported in column studies with mixed autochthonous flora from clean groundwater. The meta and para isomers of xylene and 1,2,4-trimethylbenzene were degraded more rapidly than o-xylene, 1,2,3-trimethylbenzene or 1,3,5-trimethylbenzene. These studies by Kappeler and Wuhrmann (1978a,b) make up the bulk of the work on degradation of alkyl substituted benzenes.

3.5.3 In-situ Biodegradation

Application of in-situ bioremediation technology for the renovation of hydrocarbon contaminated aquifers is based primarily on the work of Raymond et al. (1975a,b) and Raymond et al. (1977) at Suntech. Nutrients and oxygen were introduced with injection wells, and circulated through the aquifer with pumping wells. This technique and other bio-remediation methods were reviewed by Wilson et al. (1986). These authors noted that studies are needed to investigate the effectiveness of natural biorestoration and to evaluate whether enhancement of natural processes is possible or desirable.

Transport of sufficient oxygen to subsurface microbes is a major technical problem. Oxygen is only slightly soluble in water and is quickly depleted during aerobic biodegradation. Oxygen addition by air sparging, oxygen sparging and the use of hydrogen peroxide are documented in the literature (Lee and Ward, 1984). The use of hydrogen peroxide appears particularly advantageous (TRI, 1982). Hydrogen peroxide is relatively inexpensive, nonpersistent

and is more soluble in water than air or molecular oxygen.
However, it is also cytotoxic and may be chemically reduced,
especially in the presence of iron salts. The biological
decomposition of hydrogen peroxide is enzymatic:

$$2H_2O_2 \xrightarrow{\text{catalase}} 2H_2O + O_2 \qquad [3.18]$$

$$H_2O_2 + XH_2 \xrightarrow{\text{peroxidase}} 2H_2O + X \qquad [3.19]$$
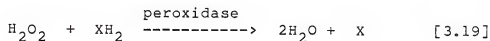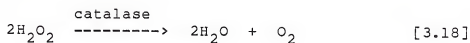
where X is a biological reducing agent. Non-enzymatic
decomposition occurs most frequently in the presence of iron
salts:

$$Fe^{++} + H_2O_2 \longrightarrow Fe^{+++} + OH^- + OH^{\cdot} \qquad [3.20]$$

$$OH^{\cdot} + H_2O_2 \longrightarrow H_2O + H^+ + O_2^{\cdot -} \qquad [3.21]$$
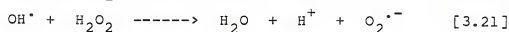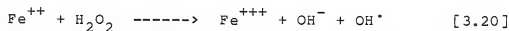
Britton (1985) reported that hydrogen peroxide was
relatively stable in combination with phosphates, even in
the presence of moderate iron concentrations, and that
bacterial populations can tolerate H_2O_2 concentrations up to
500 mg/L. Hydrogen peroxide was shown (Britton, 1985) to
increase microbial counts by 10^2, but there was no reported
increase in hydrocarbon removal.

3.5.4 Measurement of Microbial Activity

The reduction of INT (2-p-iodophenol-3-p-nitrophenyl-5-
phenyl tetrazolium chloride) to INT-formazan by the electron
transport system is a function of cell respiration, and is
widely used as a general measure of microbial activity.

This technique is recommended as an index of general microbial activity of soil microorganisms (Klein et al., 1971).

Reduction of INT to INT-formazan is a sensitive assay for dehydrogenase activity. The INT-formazan is easily extracted from sediments and soils by methanol, and the INT-formazan complex is stable. Trevors et al. (1982) found a high correlation between electron transport system activity and oxygen consumption. Klein et al. (1971) presented a rapid and simple procedure for the determination of dehydrogenase activity using INT in soils with low organic carbon.

3.6 Summary

This literature review has presented some of the basic principles required as a basis for the discussion of the experimental work reported in this dissertation, and has highlighted some of the important findings relative to the dispersion, sorption and biodegradation of aromatic compounds in groundwater systems.

CHAPTER IV
MATERIALS AND METHODS

4.1 Introduction

This chapter discusses the materials and experimental methods employed during this study. The field site, and the solutes and sorbents are described followed by a description of the chromatographic systems. Laboratory experiments for the determination of hydrolysis, sorption and biodegradation parameters are discussed. Finally, the field procedures and experiments are discussed.

4.2 Site Description

The field research site used for a portion of this study was located at the Citrus Research and Education Center (CREC) at Lake Alfred, Fl. The site was located in the Trail-Ridge Lake Wales Ridge system of hills containing deep internally drained lake basins. Unconsolidated deposits in the area consisted of sand and sandy clays up to 150 ft thick above the limestone bedrock. The geology was marked by many sinkholes formed through subsidence of the unconsolidated deposits into solution cavities in the limestone (Spangler, 1984).

The research site was located on the rim of an ancient sinkhole. The surficial aquifer was composed of sand and clayey sands. An continuous clayey confining layer of uneven depth was present between 7 to 12 ft below land surface. This layer supported a saturated zone between 3 to 6 ft in thickness. Local relief was from 156 ft (above mean sea level) at the top of the hill at the eastern boundary of the site, to 131 ft in the wetland area at the west edge of the site. A site map is shown in Figure 4-1. The surficial aquifer was comprised of medium angular grained sands and fill material. The hydrology of the site was discussed by Killan (1987).

The surficial aquifer was contaminated during the spring of 1983 by the loss of 7500-8000 gallons of leaded gasoline from a storage tank. Free floating gasoline was removed by surface skimming as of May 1985. The outline of the contaminated area as of October, 1986 is shown in Figure 4-2. The plume was defined by determination of explosive gas concentrations in bore holes throughout the site. These data were confirmed by GC analysis of soil cores and the use of ground penetrating radar. These techniques were described in detail by Killan (1987).

4.3 Aquifer Material

Aquifer materials used in this research were obtained from the field research site at the IFAS-Citrus Research and Education Center at Lake Alfred Florida. A site map is
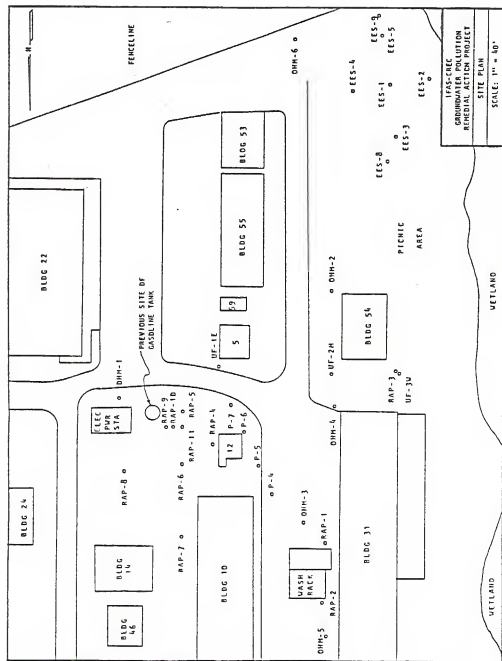
Figure 4-1. Site plan of the field research site at the Citrus Research and Education Center, Lake Alfred, FL.
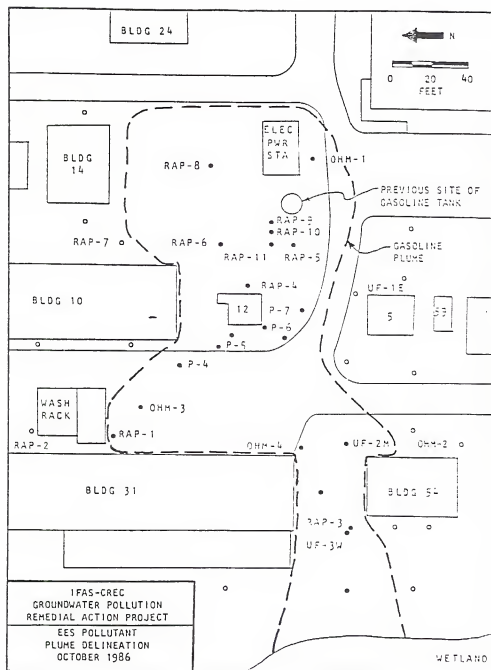
Figure 4-2. Extent of the hydrocarbon plume at the
            field research site as of October, 1986.

shown in Figure 4-1. All experiments were carried out with subsamples of the same aquifer material. The sample was collected with a stainless steel auger just below the water table at a depth of about 4 feet, approximately 10 feet east of Well RAP-1. Care was taken to avoid contamination with surface materials by removing one foot of top soil, and through careful handling of the auger. The aquifer material was oven dried at 105 C for 24 hours, sieved through 2 mm standard sieve and stored, covered, at room temperature. Prior to use, the aquifer material was autoclaved for 90 minutes on each of three consecutive days to sterilize the materials.

Prior to sterilization and drying, selected physical and chemical properties of the aquifer materials used in the laboratory studies were characterized (pH, particle density, particle size analysis, percent organic carbon, bulk density, hydraulic conductivity, and water content) using standard methods of soil analysis (Black, 1965).

4.4 Choice of Solutes

Gasoline contaminated well water from the Lake Alfred research site was used as the source of dissolved solutes for the majority of experiments in this study. With the exception of a single solute column sorption experiment with benzene spiked in to RAP-2 water, all experiments were performed with mixtures of dissolved hydrocarbons at

concentrations occurring in the field. These concentrations are the result of the solubilization and subsequent weathering of gasoline hydrocarbons into groundwater. Well OHM-4 was used as the source of water for these experiments. This well was chosen based on consistently high levels of dissolved aromatic hydrocarbons. Hydrocarbon free groundwater was obtained from a non-contaminated portion of the aquifer (Well RAP-2). Hydrocarbon concentrations in these waters were monitored monthly. Well RAP-2 remained free of aromatic hydrocarbons throughout the course of these experiments. Concentrations of aromatic hydrocarbons varied in Well OHM-4 but remained high enough to provide samples for laboratory experiments.

Water samples were collected with a 5.1 cm (2") id poly vinyl chloride (PVC) bailer, following removal of five well volumes to allow collection of a representative sample. Well volumes were calculated based on the diameter of the well, and the depth of water in the well. These water samples were collected in four liter brown glass bottles transported on ice, and stored at 4 C upon arrival at the laboratory. The pH of these well waters ranged from 6 to 7. The conductivity was approximately 300 umhos. Total phosphate was 0.4 mg/L for RAP-2 and was 0.65 mg/L for well OHM-4. Nitrate was 0.29 mg/L in well RAP-2 and 0.20 in well OHM-4.

The single solute column experiment with benzene used RAP-2 water spiked with benzene (Aldrich, gold label 99.9%) to yield a solution of 4000 ug/L benzene.

4.5 Hydrocarbon Analyses

Gas chromatographic analyses of hydrocarbons for this study were performed on two systems. These are described below.

4.5.1 GC/MS Analyses

Field samples collected before September, 1986, and the initial hydrolysis vials were analyzed for volatile aromatic constituents using a Hewlett Packard model 5985B GC/MS/COMP system equipped with a 10 port Tekmar Automatic Liquid Sampler (ALS) and Liquid Sample Concentrator (LSC) purge and trap system. EPA method 624 was used. Separation of analytes was achieved with a 0.32 mm i.d., 30 meter long, DB-5 (1 um film thickness) fused silica capillary column (J & W Scientific), with manual liquid nitrogen cryofocusing. The 1,4 isomer of dichlorobenzene was used as an internal standard. Response factors for benzene, toluene, ethylbenzene and o-xylene were determined relative to the internal standard and used for quantitation. Response factors for meta and para xylene were assumed to be the same as the ortho isomer. A response factor of 1 was assumed for the C_9H_{12} hydrocarbons. Chromatographic conditions were as follows:

```
mass range        45-450 amu
Temp 1            30 C
Temp 2            280 C
Rate              5 C/min
Hold time         10 minutes
Cryofocus time    5 minutes
Pre-cool          2 minutes
```

4.5.2 GC Analyses

Hydrocarbon analyses were performed on a Perkin Elmer model 8410 gas chromatograph with a flame ionization detector and microprocessor data system. Samples were concentrated by purge and trap with a Tekmar LSC/ALS system employing a modified version of EPA method 602. Analytical separation was achieved with a 0.53 mm i.d., 30 meter long, fused silica Megabore DB-1 (100% methylpolysiloxane) column (J & W Scientific) with a 3 um film thickness.

Benzene, toluene, ethylbenzene, o-xylene and m,p-xylene were quantified using the internal standard method (1,4 dichlorobenzene) during August and September 1986 for monthly analysis of field samples and for day = 0 hydrolysis ampules. After this date, eight isomers of C_9H_{12} were identified and confirmed by analysis of individual standards and were quantified in all chromatograms along with BTEX (benzene + toluene + ethylbenzene + m,p,o-xylene) compounds. The internal standard was changed from 1,4-dichlorobenzene to chlorobenzene to avoid co-elution problems. A complete description of this analytical method and a summary of the quality control parameters for this method are in Appendix A.

The meta and para isomers of xylene were not resolved on either chromatographic system employed in this research. The combination of these analytes was reported as m,p-xylene. Likewise, 3-ethyltoluene and 4-ethyltoluene were not resolved with the analytical system employed in this study, and the combined concentrations of these analytes were reported in this study with the abbreviation 3,4-ethyltoluene.

4.6 Hydrolysis Studies

Hydrolysis studies were performed in 5 mL glass ampules (Fisher Scientific). Ampules were rinsed with methanol and oven dried at 105 C . Ten microliters of hydrocarbon contaminated groundwater were spiked into ampules containing 5 mL of buffer solution. Buffer solutions were prepared with non contaminated well water, and the pH was adjusted to pH = 2.0, 7.0, 9.2, and 12.0 with 0.01 M phosphate buffers. The ampules were sealed with an ampule sealer (Oceanographic International, College Station, TX), and autoclaved (1 hour at 120 C). One set of ampules was analyzed at time zero. Another set of ampules was stored in the dark at 20, 40 and 60 C and analyzed by gas chromatography (GC) after 60 days.

4.7   Batch Sorption Studies

Sorption batch studies were performed in 40 mL VOA vials with Teflon coated septa (Fisher Scientific). Vials were first filled with 60 g of aquifer material, and then autoclaved at 120 C for 1 hour on each of three consecutive days.

Water from well OHM-4, containing a mixture of dissolved aromatic hydrocarbons, was used in the batch sorption experiments. As a result, all these experiments are multisolute, at concentrations representative of those found across the aquifer at Lake Alfred.

4.7.1   Sorption Experiments

Water used in the sorption experiments was filter sterilized through 0.2 um membrane filters (Gelman Metricel) and then added to each vial. The range of solute concentrations was achieved by dilution of Well OHM-4 water with Well RAP-2 water at ratios between 1:1 to 1:1000. Each dilution was performed in triplicate. Non-soil controls (solute water with no soil) were also set up in triplicate. To minimize headspace, the vials were premixed on a rotary tumbler for approximately 1 hour to remove interstitial air and to disperse the foam that formed during mixing. The vials were then opened, completely filled with sample and recapped. A high solids to solution ratio (2.9 g/ g) was used to maximize the fractional decrease in solution

concentration owing to sorption, and to more closely simulate natural aquifer conditions.

Vials used in sorption experiments were equilibrated at room temperature (20 ± 2 C) on a rotary tumbler at approximately 20 rpm for 18 hours, and then centrifuged at 800 G for 30 minutes. Samples were analyzed by purge and trap/gas chromatography. Vials used in the batch sorption kinetic rate study were sampled at 1, 2, 4, 8, 16, 24, 36 and 48 hours.

4.7.2 Desorption experiments

Desorption experiments were conducted subsequent to a sorption experiment. Following centrifugation and sampling for sorption losses, approximately 10 mL of supernatant were removed and replaced with hydrocarbon free water (Well RAP-2). The vials were re-equilibrated for 24 hours on the rotary tumbler, centrifuged and sampled. Each vial was only desorbed one time. These experiments were not designed to calculate desorption isotherms or test isotherm nonsingularity.

4.7.3 Calculation of Sorption Coefficients

The amount of solute sorbed to the aquifer material (ng solute/gram soil) was calculated by determining the difference between the solution concentration of the non-soil blanks and the soil containing vials. The amount of solute lost was divided by the solution to soil ratio to normalize the data to a ng/gram basis. Sorption coefficients were calculated by fitting isotherm data to three models; linear, linear with intercept forced through

zero, and the log normalized (Freundlich) models (Miller and Weber, 1984).

4.8 Column Sorption Studies

4.8.1 Experimental Procedures

Leaching column experiments were performed with a 25 x 250 mm glass preparative chromatography column (Altex cat. no. 252-18) with a Teflon coated adjustable plunger (Nkedi-Kizza et al., 1987). Aquifer material was dry packed into the column which was then autoclaved at 120 C for 1 hour. The solutes were pumped from 2.6 L Teflon gas sampling bags (Alltech Associates, Deerfield, IL) with a Gilson model 302 HPLC pump fitted with a model 5s pump head (Gilson Medical Electronics, Middleton, WI). The flow range of this system was 0.005 - 5.00 mL per minute. All transfer lines and connections were Teflon or stainless steel to minimize interaction of solutes with reactive surfaces. Column length was adjusted to 5.0 cm. Flow rates through the column were set at 1 ml/min (0.204 cm/min) for sorption studies. Column effluent breakthrough curves (BTCs) were measured under steady saturated water flow conditions with continuous application of solute containing water.

Effluents from the sorption columns were collected manually in 1 ml crimp seal vials. These column effluents were either analyzed immediately or stored at 4 C in 1 mL

crimp seal vials with Teflon coated septa for later analysis. All samples were analyzed within 48 hours.

The breakthrough of an unretained solute was determined for each column using calcium chloride (1 ml/min columns). Breakthrough curves were determined by spiking hydrocarbon free groundwater from Lake Alfred (RAP-2) with chloride (600 mg/L $CaCL_2$). Chloride analyses were performed with a chloridometer automatic titrator (Buchler-Cotlove). Chloride ion was not expected to be adsorbed owing to the low cation exchange capacity of the Lake Alfred soil.

Well water used in the sorption experiments was filtered through 0.2 um membrane filters (Gelman Metricel) directly into the Teflon bags. The bags were autoclaved prior to each use. Columns were saturated with filter sterilized water from well RAP-2 prior to the input of solute containing water.

4.8.2 Estimation of Retardation Factor (R) in Columns

Three methods were used to estimate the value of R from the column data. In method 1, retardation factors (R_b) were calculated by fitting the solution of Brenner (1962) to the column effluent curves. Peclet numbers used for these calculations were determined from the breakthrough of the non-retained solutes having retardation factors equal to unity. Method 2 was based on the conservation of mass principle. This method calculated retardation factors (R_a) by evaluating the area above the breakthrough curve using Simpson's Rule (Swokowski, 1975). The R_a value was assumed

equal to the area above the BTC when the effluent
concentration (C) divided by the influent concentration (C_o)
was plotted vs pore volume as described by equation [4.1]

$$R = \int_{0}^{pv_{max}} [1-C/C_o] \, dpv \qquad [4.1]$$

where pv_{max} is the total number of pore volumes displaced
through the column, and pv is pore volumes (Nkedi-Kizza et
al., 1987). This method assumed a mass balance existed in
the soil columns. The third method set the retardation
factor (R_{pv}) to equal the number of pore volumes required
for the effluent concentration of each analyte to reach 0.5
of the influent concentration. The use of this method
assumes that the breakthrough curve is symmetrical and
sigmoidal, and that equilibrium conditions exist between the
solution and sorbed concentrations during leaching through
the column (Nkedi-Kizza et al., 1987). The value of K_d was
calculated from the various R values with equation [3.10].

4.9 Hydrogen Peroxide Evaluation

The reaction rate of hydrogen peroxide in the aquifer
environment was simulated by monitoring the dissolved oxygen
(DO) (YSI model 5739 probe and YSI model 54A DO meter),
redox potential (platinum redox electrode, Fisher
Scientific) and pH (gel membrane electrode, Fisher
Scientific) of well water and aquifer material in a 3 arm
500 mL reaction flask. Contaminated well water was

equilibrated at room temperature (20 ± 2 C) in the sealed flask. Hydrogen peroxide (50%) was added undiluted in microliter quantities and at various dilutions. Aquifer material was then added to assess the ability of the material to catalyze the reaction. The 50% hydrogen peroxide stock was titrated with 0.01N potassium permanganate (Dupont, 1984) to check the strength of the stock solution. The standardized stock was then used to make the appropriate dilutions without further calibration.

4.10 Batch Biodegradation Studies

4.10.1 Experimental Procedure

Batch biodegradation experiments were performed in 40 mL VOA vials as described for the batch sorption experiments.

Well water from OHM-4 was used as the source of both dissolved aromatic hydrocarbons and bacteria in these studies. The water was not filtered prior to use. This experiment was designed to evaluate the ability of adapted groundwater bacteria to degrade mixtures of dissolved aromatic solutes at field scale concentrations. The experimental design for batch biodegradation experiment number 1 is shown in Table 4-1. Seven treatments were set up, with 15 replicate vials per treatment. Water from Well OHM-4 was added (350 mL) to a 500 mL erlenmeyer flask, and then amended with hydrogen peroxide (50%), ammonium chloride

Table 4-1. Experimental design for batch biodegradation
            experiment #1.

Treatment	Hydrogen Peroxide (mg/L)	NH_4Cl (mg/L)	Sodium Azide (mg/L)
1A	none	none	none
1B	17	none	none
1C	68	none	none
1D	none	18	none
1E	17	18	none
1F	68	18	none
1G	none	none	1.25

(Reagent grade, Fisher Scientific) and 10% (w/v) aqueous solution of sodium azide (Fisher Scientific) as outlined in Table 4-1. Triplicate samples were analyzed for each treatment at 0, 3, 7, 15, and 31 days. Treatment number 1G was a sterile control. Hydrogen peroxide was added based on data from the hydrogen peroxide evaluation experiment and on data from Britton (1985), who demonstrated that cytotoxicity was minimal at hydrogen peroxide concentrations less than 100 mg/L. Ammonium chloride was added based on data from Mitchell (1974) who found that ammonia nitrogen is assimilated quickly during microbial growth. Ammonia (as NH_4CL) was added to achieve quantities calculated to meet nitrogen requirements of the bacteria.

Biodegradation experiment number 2 was designed to evaluate the efficacy of oxygen gas in addition to hydrogen peroxide (Table 4-2). Sterile controls were maintained in treatments 2C, 2F and 2I. Ammonium chloride and hydrogen peroxide were added as in biodegradation experiment #1. Oxygen was added by bubbling O_2 gas into a closed 3 liter flask filled with 1200 mL of contaminated well water. A valve allowed for pressure relief. Water was released through a glass tube at the bottom of the flask, fitted with a teflon stopcock. Vials were filled as described in the sorption experiments. The vials used in both batch biodegradation experiments were placed in an incubator (20 ± 1 C) and inverted once every two days to provide mixing. Samples were taken at 0, 2, 7, 14, 21 and 35 days.

Table 4-2. Experimental design for batch biodegradation
experiment #2.

Treatment #	Oxygen addition	NH4Cl (mg/L)	Sodium Azide (mg/L)
2A	air	none	none
2B	air	18	none
2C	air	none	1.25
2D	60 mg/L H_2O_2	none	none
2E	60 mg/L H_2O_2	18	none
2F	60 mg/L H_2O_2	none	1.25
2G	O_2 saturation	none	none
2H	O_2 saturation	18	none
2I	O_2 saturation	none	1.25

Following sample removal for GC analysis, dissolved oxygen was measured in each batch biodegradation vial (batch experiments 1 and 2) with a YSI model 5739 DO probe and YSI model 54A DO meter (Yellow Springs Instruments Co.).

Microbial activity was assessed through the measurement of INT reduction to INT-formazan (Klein et al., 1971). Ten grams of soil from each vial were placed in sterile 50 mL Erlenmeyer flasks. Each flask was amended with 1 mL distilled water and 1.5 mL of 0.4% (w/v) aqueous solution of filter sterilized (0.2 um Gelman Metricel membrane filters) INT (Eastman-Kodak Co.). The soil was mixed with a sterile glass rod, capped with aluminum foil and incubated at 20 C for 72 hours. Sterile controls were prepared by autoclaving several flasks for 3 consecutive days for 90 minutes. Approximately 3 grams (dry weight) of soil were removed from each flask following incubation and placed in a test tube. Ten mL of methanol were added to each tube and the contents were mixed on a vortex mixer for 1 minute, then centrifuged at 800G for 20 minutes. The INT- formazan in the methanolic extract was measured spectrophotometrically at 480 nm against a methanol extract of soil containing no INT. The INT-formazan concentration was derived from a standard curve of INT-formazan in methanol.

4.10.2 <u>Calculation of Biological Rate Constants</u>

Aqueous concentration data from the batch biodegradation vials were used with the regression equations from the Freundlich fit of the batch desorption data to

calculate the amount of solute lost to sorption in each batch vial. The extent of the sorption loss correction varied with the concentration of the analyte and the sorption parameters K_{fd} and n. This correction factor added as much as 20% to the measured concentration values. These predicted losses resulting from sorption were added to the aqueous concentration for each analyte in each vial to calculate the total concentration of each solute in the vial (C_t). These C_t values were employed to obviate the need for simultaneous calculation of biodegradation on both sorbed and aqueous concentrations and any calculation of rates of sorption-desorption during biodegradation. The C_t values were used to model the biological rate coefficients. The rate data were fitted to zero order, first order, second order and mixed order rate equations (Levenspiel, 1972), and to the Thomas slope method (Thomas, 1950).

4.11 Column Biodegradation Studies

4.11.1 Experimental Procedure

Column biological degradation experiments were performed with the same column system described in section 4.8. Two flow rates were used in these experiments. These were 1 ml/min (0.680 cm/min) and 0.90 ml/hr (0.010 cm/min). Columns operated at 0.90 ml/hr were fitted with a low dead volume in-line septa. Effluent was withdrawn with a 50 ul syringe (Hamilton Co.) and analyzed immediately. Effluents

from the 1 mL/min columns were collected and analyzed as
described in section 4.8. Breakthrough curves for a non
retained solute were obtained with tritiated water (0.01 uci
^{3}H for 0.90 ml/hr columns) or $CaCl_2$ (1 ml/min columns).
Analyses of $^{3}H_2O$ effluents were performed on a Delta 300
model 6890 Liquid Scintillation Counter (Cearle Analytical)
using Scintiverse II scintillation cocktail (Fisher
Scientific). Columns operated for biodegradation
experiments were set up in the same manner as the sorption
columns. Solute containing water was filtered through 0.45
um membrane filters (Gelman Metricel) to remove
particulates. A standing microbial population was developed
in the columns operated at 1 ml/min by inoculation with
water from well OHM-4.

4.11.2 Calculation of Rate Constants

Rate constants for the biological degradation of
aromatic solutes from column breakthrough curves were
determined by application of the first order rate equation
to the breakthrough curve data at steady state. Microbial
degradation processes are often assumed to be first order
(Bossert and Bartha, 1984). Substitution of equation [3.18]
into equation [3.11] incorporates the degradation term into
the one dimensional mass transport equation:

$$R \, \partial C / \partial t \ = D_h \, \partial^2 C / \partial x^2 - v \, \partial C / \partial x - k \, C \qquad [4.2]$$

Dividing all terms of equation [4.2] through by R and defining $D_* = D/R$, $v_* = v/R$ and $k_* = k/R$, equation [4.2] becomes

$$\partial C / \partial t = D_{h*} \, \partial^2 C / \partial x^2 - v_* \, \partial C / \partial x - k_* \, C \qquad [4.3]$$

at steady state conditions where $\partial C / \partial t = 0$, equation 4.3 reduces to:

$$D_h \, \partial^2 C / \partial x^2 - v \, \partial C / \partial x + k \, C = 0 \qquad [4.4]$$

For steady state conditions there is no sorption effect since the R term cancels out and the rate of biodegradation (k) may then be calculated by application of the first order rate equation to the portion of the BTC which is at steady state. The first order rate equation for this system is:

$$C/C_o = e^{-kt} \qquad [4.5]$$

For a column of length x, and with a pore water velocity of v, time may be expressed as

$$t = x/v \qquad [4.6]$$

and substitution of [4.6] into [4.5] and rearrangement allows calculation of the rate constant for biodegradation:

$$k = - (\ln C/C_o) \, v/x \qquad [4.7]$$

Average C/C_o values were calculated from the regions of the solute breakthrough curves where $\partial C/\partial t = 0$. This derivation assumes that microbial degradation occurs only from the aqueous phase, and that dispersion is negligible.

4.12 Field Studies

4.12.1 Aquifer Characterization

A tracer experiment was conducted to measure seepage velocities and obtain better estimates of aquifer hydraulic conductivity and field scale dispersion. RAP-9 was used as the dosing well. The following steps outline the experimental procedure:

1. A tracer solution was prepared by dissolving 50 lb (23 kg) of technical grade ammonium chloride in 55 gal (208 L) of tap water. The resulting concentration was 109,000 mg/L ammonium chloride.

2. The ammonium chloride solution was injected into the dosing well and simultaneously diluted with tap water at a metered rate of 1 gallon per minute (gpm). Dosing continued for 15.8 hours, resulting in a total dose volume of 1,035 gallons of tracer solution.

3. Detection of the tracer was monitored in wells RAP-10 and RAP-11 using a conductivity meter with a field probe. Measurements were obtained at one half- to one-hour intervals for the first 24-hour period. Wells P-

6, P-7, UF-1E, RAP-4, OHM-4, UF-2M and UF-3W were also monitored periodically for the following two weeks.

The breakthrough of the tracer was calculated in pore volumes using the equation

$$pv = vt/L \qquad [4.8]$$

where pv is pore volumes, t is time (hours), L is the distance between RAP-9 and RAP-10 (5 ft) and v is the seepage velocity (ft/hour) from work by Killan (1987).

4.12.2 Water Quality Monitoring

Samples for hydrocarbon analysis were taken from selected monitoring wells monthly from February 1, 1986 to June 1987. Sampling procedures are detailed in Appendix B. Hydrocarbon analyses were as described previously using the three chromatographic methods as they became available. The pH, temperature, dissolved oxygen, and conductivity were measured periodically in selected wells. Sampling procedures are detailed in Appendix B.

Total phosphorus concentrations were determined in all monitoring wells (EPA method 365.1). All phosphorus forms were converted to orthophosphate by autoclaving with potassium permanganate in an acidic medium. Orthophosphate was determined spectrophotometrically at 880 nm with a Perkin Elmer model 552 spectrophotometer.

Chloride was determined colorometrically in each monitoring well over several months to determine background levels of chloride via EPA method 325.1. Average background concentrations were 20 ± 8 mg/L. Nitrate was measured with

an Orion nitrate electrode via standard method 418b (APHA, 1980).

4.12.3 Microbial analyses

Viable microbial cells were enumerated by plate count technique using dilute soil extract agar (DSEA) media. This technique was developed based on work by Ghiorse and Balkwill (1983) and Wilson et al. (1983).

DSEA was prepared by autoclaving 100 g of surface soil in 100 mL of distilled water for one hour at 120 C. The supernatant was filtered (Whatman glass fiber filters) to remove particulates and diluted ten fold with distilled water and amended 1.5% (w/v) with agar (Fisher Scientific).

Ten grams of subsurface material were suspended aseptically in 100 mL 0.1% sodium pyrophosphate (Fisher Scientific) then appropriate dilutions were plated in triplicate on DSEA media. All plates were incubated aerobically at 27-30 C for ten days.

CHAPTER V
RESULTS AND DISCUSSION

5.1 Introduction

This chapter will review the results of all experiments
performed as part of this dissertation research. The
presentation of results and the interpretation of the data
for each major experimental section are grouped together to
avoid loss of continuity. Hydrolysis of aromatics in
groundwater is discussed first, followed by the results and
discussion of the batch and column sorption experiments.
Batch and column biodegradation experiments are addressed
next, followed by the presentation of field data, and the
correlation of field data with laboratory experiments.

5.2 Hydrolysis of Aromatic Hydrocarbons

The results of initial measurements (time = 0) of the
hydrolysis ampules were inconclusive, resulting from over-
dilution of the samples. Several analytes were below the
limit of detection of the GCMS analytical system, therefore
no conclusive statements may be made relative to the rates
of aromatic hydrolysis.

Statistical analysis of data from ampules after 60 days
of temperature controlled storage indicated that for a given
temperature, there was no significant (student's t-test,

0.05 level) change in concentration of analytes over the pH range tested (pH 2,7,9,12).

Only one compound, 1,2,3-trimethylbenzene, demonstrated a significant (student's t-test, 0.01 level) temperature effect at pH values of 7,9 and 12. This change in concentration occurs only at 40 C, and the concentration values at 20 and 60 C are equivalent for all pH values. These data are not consistent with data from other aromatic compounds in this study, which showed no change in concentration with varying temperatures. The apparent loss of solute seen for 1,2,3-trimethylbenzene was likely the result of working near the detection limit of the analytical system, or the result of experimental error.

The absence of concentration differences across a wide range of pH and temperature for the 60 day ampules implies that hydrolysis was not a significant mechanism for removal of aromatic hydrocarbons. This was expected, owing to the resistance of aromatic structures to nucleophilic attack by water. This results from the electronegativity associated with the delocalization of electrons in the pi bonds of the aromatic nucleous. McCarty (1984) has noted that chemical hydrolysis may occur, but that for most compounds this process was slow relative to biological removal rates. In addition, hydrolysis results in simple changes in the molecular structure, whereas biological transformations often result in the mineralization of organic compounds to carbon dioxide and water.

5.3   Characterization of Aquifer Materials

An analysis of a sub-sample of the aquifer materials
used in the laboratory experiments is presented in Table 5-
1. All experiments with aquifer material were performed
with subsamples of well-mixed aquifer material. Single size
fractions of aquifer material were not used since
extrapolation from one size fraction to another has been
shown to lead to errors in the estimation of sorption values
(Abdul et al., 1986). Unwashed, natural sorbent material
from the Lake Alfred site was used in this study to more
closely approximate field conditions. The organic carbon
content of this material was low, and particle size analysis
indicated the dominance of fine to medium grained sands.
The pH of the aquifer material was in the range suitable for
biological degradation, and was consistent with the pH
values in the well water.

5.4   Batch Sorption Studies

5.4.1   Sorption Rate Studies

Rate studies were conducted to determine the sorption
kinetics of the selected aromatic solutes with Lake Alfred
aquifer material. These experiments established the
equilibration time for the sorption isotherms. The approach
to equilibrium is shown in Figure 5-1. These curves are

Table 5-1. Selected physical and chemical Properties
            of the Lake Alfred aquifer material.

```
------------------------------------------------------------
Parameter                      Value
============================================================
```

Parameter	Value
pH	7.4 (0.01M $CaCl_2$)
Particle Density	2.6 g/mL
Water Content (by weight)	24%
Organic Carbon	0.015%
Bulk Density	1.4 g/mL
Particle Size Analysis	
clay	1.8%
silt	1.7%
very fine sand	3.0%
fine sand	38.2%
medium sand	47.0%
coarse sand	8.2%
very coarse sand	0.2%

```
------------------------------------------------------------
```
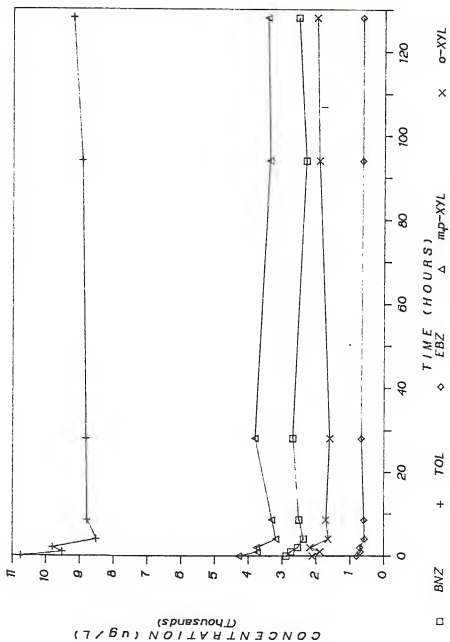
Figure 5-1. Approach to equilibrium for several aromatic solutes on Lake Alfred aquifer material.

marked by an initial rapid sorption, and equilibrium conditions are established within several (4 to 8) hours. These data are in agreement with Weber et al. (1983) who stated that sorption reactions with natural sorbents were generally rapid and not rate limited. Based on these data an equilibration time of 18 hours was chosen. Eighteen hours was chosen to maximize the time for sorption yet minimize the time for losses from the system (ie., via diffusion of solutes through the Teflon septum). This was equivalent to time scales used in previous studies (Chiou et al., 1979, 1983; Schwarzenbach and Westall, 1981). Longer equilibration times were not possible using this experimental technique since losses in non-soil blanks after 3 days made it difficult to differentiate between sorption and loss from the system. The equilibration time used in this study did not guarantee that the sorption process was complete, but that it was complete to the extent that it could be accurately measured.

5.4.2 <u>Batch Sorption Isotherm Data</u>

Data for the equilibrium batch sorption isotherms are presented in Appendix C. Solution concentrations are in ug/L, and sorbed concentrations are in ng/g. Three models were fitted to these data using the method of least squares regression analysis. These models were the linear, linear with suppressed fit (forced through the origin), and the Freundlich (log-log transformed). The results of these analyses for the linear models are presented in Table 5-2

Table 5-2. Regression parameters for the analysis of average values of equilibrium batch isotherm sorption data with the linear model.

Compound	N^a	c_{max}^b (ug/L)	K_d, std^c	y-int^d, std	r^2
Benzene	14	950	0.066, 0.005	1.5, 4.28	0.914
Toluene	14	4200	0.049, 0.010	10.9, 65.6	0.694
m,p-Xylene	16	4300	0.095, 0.005	3.4, 28.7	0.961
o-Xylene	16	2500	0.097, 0.004	3.1, 10.8	0.979
3 or 4 ET^e	11	935	0.087, 0.012	3.8, 12.6	0.861
1,3,5-TMB^f	11	460	0.142, 0.008	1.6, 3.92	0.973
2-ET^g	11	373	0.106, 0.011	0.81, 4.66	0.910
1,2,4-TMB^h	10	1600	0.131, 0.006	4.6, 10.6	0.981
1,2,3-TMB^i	10	558	0.124, 0.010	1.7, 6.10	0.951

^{a}number of data points

^{b}maximum concentration

^{c}standard deviation

^{d}y-intercept

^{e}3 or 4 Ethyltoluene

^{f}1,3,5-Trimethylbenzene

^{g}2-Ethyltoluene

^{h}1,2,4-Trimethylbenzene

^{i}1,2,3-Trimethylbenzene

and Table 5-3. The Freundlich regression parameters are presented in Table 5-4.

There is no significant difference (student's t-test, 0.05 level) between sorption coefficients predicted with the linear model and those predicted with the linear model with suppressed intercept. The sorption coefficients are determined form the slope of the linear isotherms. In addition, statistical determination of the confidence intervals of the y-intercepts indicate that there is no significant difference between the predicted value of the y-intercept in the linear model and zero at the 0.05 significance level, confirming that these two models are analogous. Equivalence between these two models is expected since the sorbed concentration should equal zero when no solute is added to the system. A non zero intercept is an indication of nonlinearity in the isotherm. In most cases both linear models fit the data well as evidenced by the relatively high coefficients of determination (r^2). Based on these analyses, the isotherms for the sorption of aromatic solutes from Lake Alfred water onto Lake Alfred aquifer material were concluded to be linear. The coefficients of determination for toluene in both linear models were substantially lower than for other compounds in this study. The linear model with suppressed intercept accounted for only 63.6% of the total sum of squares deviations about the means for the 14 values in the toluene isotherm. This suggested that this model was not

Table 5-3. Regression parameters for the analysis of average values of equilibrium batch isotherm sorption data with the linear model (suppressed intercept).

Compound	N[a]	C_{max}[b] (ug/L)	K_d, std[c]	y-int[d]	r^2
Benzene	14	950	0.069, 0.005	0	0.904
Toluene	14	4200	0.051, 0.009	0	0.636
m,p-Xylene	16	4300	0.096, 0.004	0	0.960
o-Xylene	16	2500	0.099, 0.003	0	0.978
3 or 4 ET[e]	11	935	0.093, 0.010	0	0.850
1,3,5-TMB[f]	11	460	0.146, 0.007	0	0.969
2-ET[g]	11	373	0.108, 0.009	0	0.908
1,2,4-TMB[h]	10	1600	0.135, 0.005	0	0.978
1,2,3-TMB[i]	9	558	0.128, 0.008	0	0.948

[a] number of data points

[b] maximum concentration

[c] standard deviation

[d] y-intercept

[e] 3 or 4 Ethyltoluene

[f] 1,3,5-Trimethylbenzene

[g] 2-Ethyltoluene

[h] 1,2,4-Trimethylbenzene

[i] 1,2,3-Trimethylbenzene

Table 5-4. Regression parameters for the analysis of
average values of equilibrium batch isotherm
data with the Freundlich model.

Compound	N^a	c_{max}^b $(\mu g/L)$	$\log K_f$,	$\log std^c$	n^d	std^e	r^2
Benzene	14	950	-0.857,	0.217	0.901,	0.071	0.952
Toluene	14	4200	-0.783,	0.260	0.876,	0.076	0.917
m,p-Xylene	16	4300	-0.758,	0.110	0.916,	0.031	0.984
o-Xylene	16	2500	-0.873,	0.098	0.966,	0.026	0.990
3 or 4 ET^f	11	935	-0.702,	0.158	0.904,	0.054	0.958
1,3,5-TMB^g	11	460	-0.605,	0.081	0.921,	0.029	0.991
2-ET^h	11	373	-0.951,	0.255	0.993,	0.088	0.934
1,2,4-TMB^i	10	1600	-0.641,	0.099	0.937,	0.035	0.989
1,2,3-TMB^j	9	558	-0.623,	0.078	0.918,	0.028	0.995

[a] number of data points

[b] maximum concentration

[c] log standard deviation of K_f values

[d] Freundlich exponent

[e] standard deviation of Freundlich exponent

[f] 3 or 4 Ethyltoluene

[g] 1,3,5-Trimethylbenzene

[h] 2-Ethyltoluene

[i] 1,2,4-Trimethylbenzene

[j] 1,2,3-Trimethylbenzene

appropriate for estimation of sorption. However, analysis of variance with a global F-test indicated that the model was useful for predicting sorption at the 0.01 significance level. Therefore, the linearity of all isotherms was confirmed. Linear isotherms have been noted by several authors (Schwarzenbach and Westall, 1981, Chiou et al., 1979, Karickhoff et al., 1979) and the data presented in this study are in agreement with these studies.

Curtis et al. (1986) noted that the use of the linear regression technique was not statistically rigorous since variance in the dependent variable was not distributed uniformly across the observed concentration range. These authors suggested that a least squares fit on the log transformed data (Freundlich model) gives a better approximation by providing a more uniform distribution of variance. The Freundlich model provided a good fit to the data in this study (Table 5-4) as evidenced by the high coefficients of determination for the Freundlich model. The Freundlich isotherm explained between 91.7 to 99.5% of the variance in the data, and provided a slightly improved fit to the isotherm data relative to the linear models. The r^2 value for toluene was 0.917, which was much improved over the coefficient of determination for toluene in the linear model. The log K_f values for the study compounds are also presented in Table 5-4. Values for several components (ethylbenzene, and the propylbenzenes) were not included in the table owing to their low concentrations in Well OHM-4

water on the day samples were collected for this study. The linearity of these isotherms was confirmed by the values of the regression coefficients and the Freundlich exponents (n), both of which were close to unity. As n approaches unity the models should converge since the linear model is in effect a special case of the Freundlich model.

A comparison of the Freundlich and linear models is presented in Table 5-5. The deviation between predicted amounts of sorption for the linear model with suppressed intercept and Freundlich models are expressed as ratios between the calculated sorbed concentrations. This method was used to evaluate the predictive equivalence of both models over the concentration ranges encountered in this study. This method was chosen, since direct comparison of K_d and K_f values may be misleading owing to the log transformation of the data in the Freundlich isotherm model. The largest deviations occurred for toluene at 1 ug/L. In general the ratios approached unity as the concentrations increased, but diverged in the range between 1 to 50 ug/L. This comparison indicates that the models, were essentially similar, as is predicted from the values of the Freundlich exponent (n). As n approaches unity, the Freundlich isotherm approaches the linear isotherm. The convergence of these models is confirmed by an examination of 2-ethyltoluene in Table 5-5. This compound has the highest Freundlich constant (n = 0.993) and the ratios of predicted

Table 5-5.   Ratio of sorbed concentrations calculated
             from Freundlich and linear equilibrium models

Solute	concentrations (ug/L)				
	1	50	100	500	1000
Benzene	2.01[a]	1.73	1.27	1.09	1.01
Toluene	3.23	1.97	1.81	1.48	1.36
m,p-Xylene	1.81	1.30	1.23	1.08	1.01
o-Xylene	1.35	1.18	1.16	1.09	1.07
3 or 4 ET[b]	2.14	1.48	1.38	1.18	1.10
1,3,5-TMB[c]	1.70	1.25	1.18	1.04	0.99
2-ET[d]	1.04	1.01	1.00	0.99	0.98
1,2,4-TMB[e]	1.69	1.34	1.28	1.15	1.10
1,2,3-TMB[f]	1.88	1.35	1.27	1.12	1.05

[a] the ratio of the amount sorbed as calculated from the
Freundlich model to the amount sorbed predicted from the
linear model with suppressed intercept, at the same
solution concentration.

[b] 3 or 4 Ethyltoluene

[c] 1,3,5-Trimethylbenzene

[d] 2-Ethyltoluene

[e] 1,2,4-Trimethylbenzene

[f] 1,2,3-Trimethylbenzene

sorption from the two models are consistently close to one over the entire concentration range tested.

Freundlich isotherms for benzene and toluene are shown in Figures 5-2 and 5-3. Graphs of Freundlich isotherms for the remaining solutes are presented in Appendix C. Average values are plotted in Figures 5-2 and 5-3 and error bars showing one standard deviation in the experimental determination of the sorbed concentrations are presented to give an indication of the variance in these data. Standard deviations for all compounds are shown in Appendix C. The influence of dissolved organic carbon was not assessed during this study. However, based on the work of Curtis et al., (1986) with a sandy aquifer material (0.02% organic carbon), organic carbon in this study was not expected to decrease the values of K_d by more than 5%. Water from the Lake Alfred aquifer was used in these experiments, and the organic carbon in solution was assumed to be in equilibrium with the organic carbon on the aquifer material. Therefore, dissolution of additional organic carbon into solution should have been minimal, and K_d should not be greatly affected. This hypothesis was confirmed by evaluation of the partitioning model as a predictive technique for sorption of aromatic solutes to the Lake Alfred aquifer material in section 5.6. The interaction between organic carbon and the solutes was shown to be low.
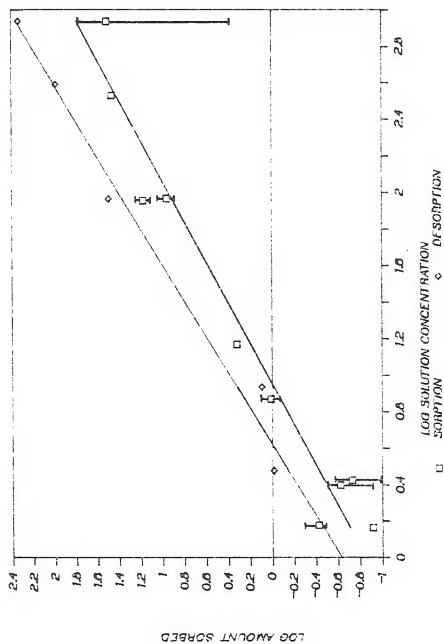
Figure 5-2. Freundlich sorption isotherm for benzene at equilibrium.
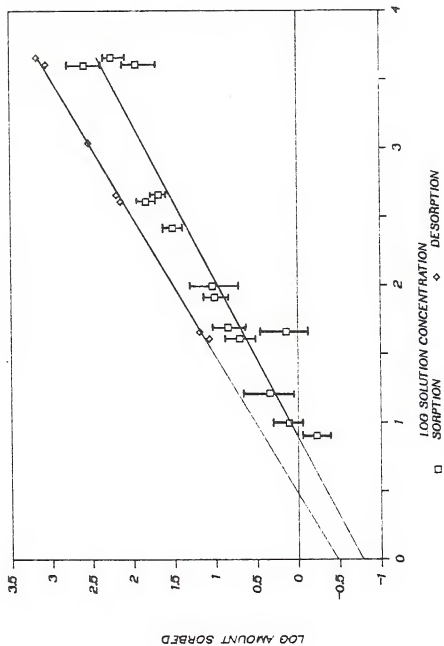
Figure 5-3. Freundlich sorption isotherm for toluene at equilibrium.

5.4.3 Batch Desorption Experiments

Desorption data are also presented in Figures 5-2 and 5-3, fit with the Freundlich type model. Visual inspection of the desorption data suggests some degree of irreversibility or some difference in desorption kinetics based on the upward displacement of the desorption regression lines. However, the calculated values of the partition coefficient for desorption with the linear type model (Table 5-6) and for the linear type model with suppressed intercept (Table 5-7) were not significantly different from sorption values (K_d) at the 0.05 probability level. Desorption coefficients from the Freundlich type model (K_{fd}) were also not significantly different from K_f values at the 0.05 level (Table 5-8). Statistical analyses of the models used to evaluate the desorption coefficients indicated that all three models gave excellent fit to the data, as evidenced by the high coefficients of determination.

These data suggested the reversibility of the sorption process, and demonstrated that the hysteretical behavior of the desorption data were not significant. This was consistent with a majority of the published literature on sorption of organic compounds to natural sorbents (Miller and Weber, 1984).

For purposes of discussion, the K_d values from the linear model with suppressed intercept are used in the following sections. As discussed earlier, these data were

Table 5-6. Regression parameters for the analysis of average values of equilibrium batch desorption data with the linear model.

Compound	N^a	c_{max}^b (ug/L)	K_{dd}, std^c	y-int^d std	r^2
Benzene	5	950	0.248, 0.006	2.2, 4.18	0.998
Toluene	8	4200	0.303, 0.011	4.13, 55.8	0.992
m,p-Xylene	9	4300	0.186, 0.006	13.3, 30.1	0.993
o-Xylene	9	2500	0.152, 0.012	11.0, 31.1	0.955
3 or 4 ET^e	9	935	0.250, 0.018	-2.9, 18.4	0.968
1,3,5-TMB^f	8	460	0.194, 0.004	1.5, 1.62	0.998
2-ET^g	7	373	0.566, 0.010	0.78, 2.64	0.999
1,2,4-TMB^h	10	1600	0.199, 0.005	3.3, 7.62	0.996
1,2,3-TMB^i	9	558	0.219, 0.032	1.1, 20.3	0.871

^{a}number of data points

^{b}maximum concentration

^{c}standard deviation

^{d}y-intercept

^{e}3 or 4 Ethyltoluene

^{f}1,3,5-Trimethylbenzene

^{g}2-Ethyltoluene

^{h}1,2,4-Trimethylbenzene

^{i}1,2,3-Trimethylbenzene

Table 5-7. Regression parameters for the analysis of average values of equilibrium batch desorption data with the linear model (suppressed intercept).

Compound	N^a	C_{max}^b (ug/L)	K_{dd}, std^c	y-int^d	r^2
Benzene	5	950	0.251, 0.004	0	0.998
Toluene	8	4200	0.304, 0.008	0	0.992
m,p-Xylene	9	4300	0.190, 0.005	0	0.992
o-Xylene	9	2500	0.159, 0.010	0	0.951
3 or 4 ET^e	9	935	0.256, 0.014	0	0.967
1,3,5-TMB^f	8	460	0.1968 0.003	0	0.997
2-ET^g	7	373	0.570, 0.007	0	0.999
1,2,4-TMB^h	10	1600	0.202, 0.004	0	0.996
1,2,3-TMB^i	9	558	0.221, 0.022	0	0.870

^{a}number of data points

^{b}maximum concentration

^{c}standard deviation

^{d}y-intercept

^{e}3 or 4 Ethyltoluene

^{f}1,3,5-Trimethylbenzene

^{g}2-Ethyltoluene

^{h}1,2,4-Trimethylbenzene

^{i}1,2,3-Trimethylbenzene

Table 5-8. Regression parameters for the analysis of
average values of equilibrium batch
desorption data with the Freundlich model.

Compound	N^a	C_{max}^b (ug/L)	log log K_f, std^c	n^d, std^e	r^2
Benzene	5	950	-0.635, 0.168	1.02, 0.079	0.982
Toluene	8	4200	-0.478, 0.039	0.992, 0.019	0.998
m,p-Xylene	9	4300	-0.561, 0.096	0.963, 0.043	0.986
o-Xylene	9	2500	-0.159, 0.263	0.774, 0.099	0.891
3 or 4 ET^f	9	935	-0.692, 0.068	1.029, 0.030	0.994
1,3,5-TMB^g	8	460	-0.569, 0.051	0.956, 0.025	0.996
2-ET^h	7	373	-0.657, 0.079	0.983, 0.046	0.989
1,2,4-TMB^i	10	1600	-0.658, 0.122	0.997, 0.056	0.981
1,2,3-TMB^j	9	558	-0.624, 0.092	0.988, 0.038	0.990

^{a}number of data points

^{b}maximum concentration

^{c}log standard deviation of K_f values

^{d}Freundlich exponent

^{e} standard deviation of Freundlich exponent

^{f}3 or 4 Ethyltoluene

^{g}1,3,5-Trimethylbenzene

^{h}2-Ethyltoluene

^{i}1,2,4-Trimethylbenzene

^{j}1,2,3-Trimethylbenzene

or linear models, and this model is more convenient for the application of equation [3.10].

5.5 Breakthrough Curves for Aromatic Solutes

5.5.1 Measurement of Column Dispersion

Breakthrough curves (BTCs) for a non-retained solute were determined for each column used in these experiments. Analysis of these data allowed the determination of the Peclet number used to model the breakthrough of the aromatic solutes. Evaluation of these data also allowed the calculation of dispersion in the column. Chloride and tritiated water were used in these experiments.

Dispersion (D_h) was calculated from the slope of a plot of C/Co vs pore volumes (pv) at pv = 1 according to the equation (Rao, 1985):

$$D_h = [v L/ 4\ pi\ B^2] \qquad [5.1]$$

where D_h is the hydrodynamic dispersion coefficient (cm^2/min), v is the flow velocity (cm/min), L is the length of the column (cm) and B is the slope of the BTC at C/Co =1. This assumes a sigmoidal shaped curve, and this assumption was valid for these breakthrough curves. A typical breakthrough curve is shown in Figure 5-4. Some values of D_h are presented in Table 5-9. Columns with flow rates of 1 ml/min exhibited higher values of D_h since dispersion
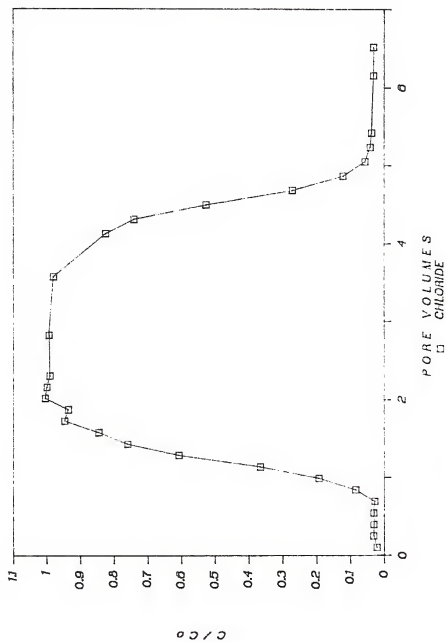
Figure 5-4. Breakthrough curve for chloride for a 5 cm sorption column.

Table 5-9. Values of dispersion coefficients calculated
            from the breakthrough curves of unretained
            solutes in laboratory columns.

Tracer	Flow (mL/min)	Velocity (cm/min)	Dispersion (D_h) (cm^2/min)	avg[a]	std[b]
^3H_2O	0.015	0.003	0.00053		
^3H_2O	0.015	0.003	0.00066		
^3H_2O	0.015	0.003	0.00040		
				0.00053	0.00013
$CaCl_2$	1.0	0.204	0.051		
$CaCl_2$	1.0	0.204	0.013		
$CaCl$	1.0	0.204	0.069		
				0.044	0.029

[a] average values of dispersion measurements

[b] standard deviation of dispersion measurements

ml/min exhibited higher values of D_h since dispersion increases with increasing pore water velocity (Roberts et al., 1985). It may be noted that the pore water velocity of 0.680 cm/min was equivalent to the seepage velocity in some portions of the aquifer at the Lake Alfred field site. These data are compared to field dispersion data in section 5.10.

5.5.2 Aromatic Solute Breakthrough Curves

Breakthrough curves for selected, dissolved aromatic solutes in the column effluent (Well OHM-4 water) are shown in Figure 5-5 (benzene) Figure 5-6 (toluene) and Figure 5-7 (n-propylbenzene). Breakthrough curves for these solutes are presented because they show the the breakthrough of the least retained compounds (benzene and toluene) and the most retained (n-propylbenzene). These solutes are presented separately to avoid overlap on a single plot, but are part of the multi-component mixture resulting from the solubilization of gasoline into groundwater at the Lake Alfred site. Graphical representations of the remaining solutes in the column effluent are shown in Appendix D. The changes in effluent concentration near the end of each breakthrough curve was consistent for each solute, reflecting the same relative variability. These deviations may be explained by heterogeneities in flow paths in the porous media, or by analytical error.

Calculated values of R, K_d, and K_{oc} based on the analyses of the column data by curve fitting to Brenner
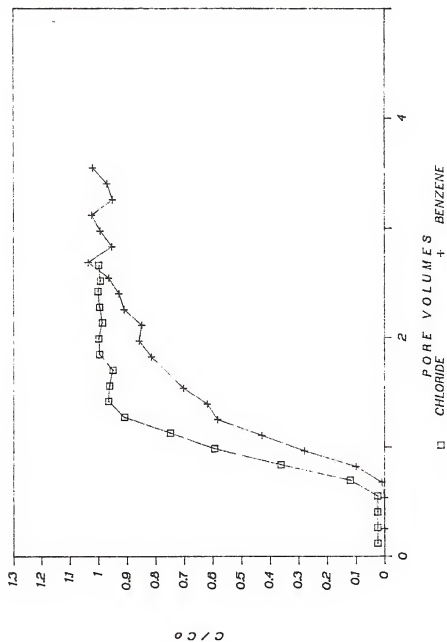
Figure 5-5. Breakthrough curve for benzene from Lake Alfred water (C_o = 4700 ug/L)
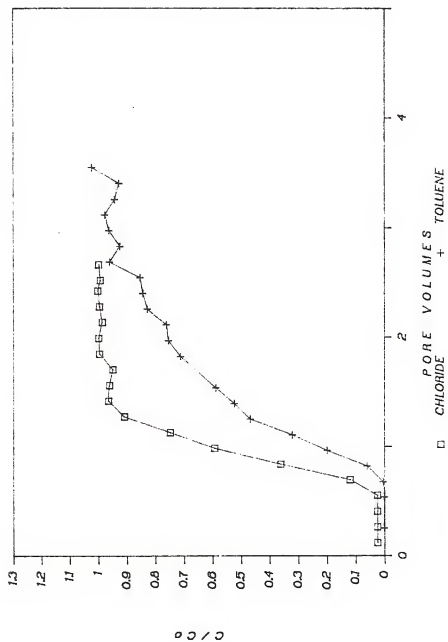
Figure 5-6. Breakthrough curve for toluene from Lake Alfred water (C_O = 2600 ug/L).
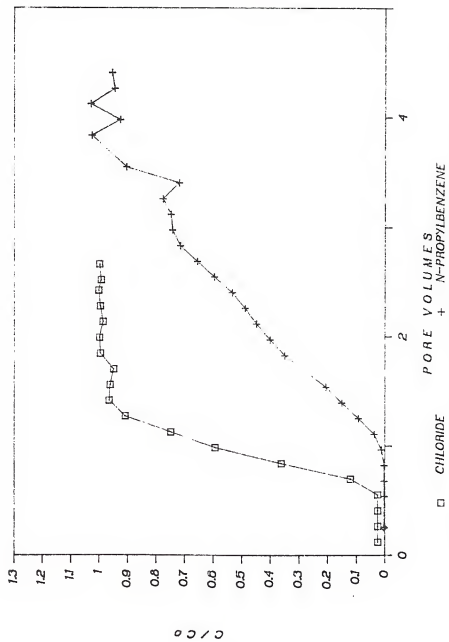
Figure 5-7 Breakthrough curve for n-propylbenzene from Lake Alfred water (C_o = 1000 ug/L).

(1962) are shown in Table 5-10. Breakthrough curve data are compiled in Appendix D.

Retardation factors for these solute breakthrough curves were also evaluated by estimating the area above the curve using Simpson's method. This method of calculation yielded R values which were slightly greater than the fitted values (Table 5-11), but which exhibited the same relative elution order. The R values calculated from the area above the BTC were within 0.1 of the values calculated by curve fitting. Retardation factors were also calculated by determination of the number of pore volumes required to reach C/C_o value of 0.5. All three methods of calculation are compared in Table 5-11. The breakthrough curves for the solutes in this study were slightly asymmetrical whereas the curves for the unretained solute were sigmoidal and symmetrical. This asymmetry was attributed to sorption nonequilibrium during transport through the column and not to dispersion. The shape of the measured BTC is determined by the kinetics of the sorption-desorption process. Symmetrical BTC are obtained when the sorption process is instantaneous and equilibrium conditions exist between sorbed and aqueous concentrations. Under non-equilibrium conditions during flow, asymmetrical BTC are obtained (Rao and Davidson, 1979). This type of response has been reported by several investigators for pesticide breakthrough (Nkedi-Kizza et al., 1987).

Table 5-10 . Calculated values of R, K_d and K_{oc} from analysis of solute breakthrough curves.

Compound	C_{inf}[a]	R[b]	K_d[c]	K_{oc}[d]	log K_{oc}
Benzene	4700	1.36	0.059	393	2.60
Toluene	2600	1.55	0.091	607	2.78
Ethylbenzene	1800	1.65	0.107	713	2.85
m,p-Xylene	1700	1.85	0.140	933	2.97
o-Xylene	2200	1.60	0.099	660	2.82
Isopropylbenzene	1000	2.00	0.165	1100	3.04
n-Propylbenzene	560	2.40	0.231	1540	3.19
3 or 4 Ethyltoluene	1600	2.25	0.206	1373	3.14
1,3,5-TMB[e]	530	2.15	0.190	1267	3.10
2-Ethyltoluene	990	1.90	0.148	987	2.99
1,2,4-TMB[f]	770	2.10	0.181	1207	3.08
1,2,3-TMB[g]	1223	1.84	0.138	920	2.96

[a] influent concentration

[b] calculated by curve fitting with Brenner (1962) with P_e = 8.

[c] calculated from the relationship $K_d = (R-1) \theta / p$ where $\theta = 0.30$ and $p = 1.82$

[d] $K_{oc} = K_d / f_{oc}$ where $f_{oc} = 0.00015$.

[e] 1,3,5-Trimethylbenzene

[f] 1,2,4-Trimethylbenzene

[g] 1,2,3-Trimethylbenzene

Table 5-11. Retardation factors calculated from leaching
column and equilibrium batch isotherm data

Compound	R_a [a]	R_{pv} [b]	R_i [c]	R_b [d]
Benzene	1.45	1.17	1.60	1.36
Toluene	1.73	1.33	1.72	1.55
Ethylbenzene	1.73	1.49	nd [e]	1.65
m,p-Xylene	1.99	1.66	1.76	1.85
o-Xylene	1.68	1.39	1.58	1.60
Isopropylbenzene	2.08	1.82	nd	2.00
n-Propylbenzene	2.49	2.29	nd	2.40
3 or 4 Ethyltoluene	2.32	2.05	1.86	2.25
1,3,5-Trimethylbenzene	2.26	2.02	1.94	2.15
2-Ethyltoluene	2.02	1.74	1.49	1.90
1,2,4-Trimethylbenzene	2.20	1.92	1.99	2.10
1,2,3-Trimethylbenzene	1.93	1.67	2.03	1.84

[a] R_a retardation factor calculated from the area of the
breakthrough curve.

[b] R_{pv} retardation factor calculated from the number of pore
volumes at $C/C_o = 0.5$

[c] R_i retardation factor calculated from equilibrium batch
isotherm data.

[d] R_b retardation factor calculated from fitting column data
to the solution of Brenner (1962).

[e] not determined

Nkedi-Kizza et al. (1987) presented a method to assess the asymmetry in a BTC by measuring the difference in the R values calculated by the pore volume method (R_{pv}), from those calculated from the area above the BTC (R_a). An empirical index for sorption nonequilibrium (ISNE) was defined as:

$$ISNE = [(R_a - R_{pv}) / R_a] \qquad [5.2]$$

where R_a is the retardation factor calculated from the area above the BTC and R_{pv} is the retardation factor calculated by evaluation of the number of pore volumes required for the column effluent to equal 0.5 of the influent concentration. For ISNE equal to zero, R_a is equal to R_{pv}, and for ISNE equal to 1, R_a is much less than R_{pv}. The calculated values of ISNE for all 12 compounds in this study are presented in Table 5-12. Based on these data, the solutes in this study do not show an appreciable amount of sorption non-equilibrium. These solutes are not strongly sorbed, and thus are not expected to exhibit a large degree of non-equilibrium. Regression of R_a values with ISNE values yielded a model with a r^2 value of 0.57. Statistical analysis of this regression model indicated that the model was useful for predicting ISNE from R_a values at the 0.01 significance level.

The cause of nonequilibrium may be the result of several physical or chemical phenomena which limit the rate

Table 5-12. An empirical index of sorption nonequilibrium (ISNE) for 12 selected aromatic solutes leaching through Lake Alfred aquifer material.

Compound	ISNE
Benzene	0.20
Toluene	0.23
Ethylbenzene	0.14
m,p-Xylene	0.17
o-Xylene	0.17
Isopropylbenzene	0.13
n-Propylbenzene	0.10
3 or 4 Ethyltoluene	0.12
1,3,5-Trimethylbenzene	0.11
2-Ethyltoluene	0.10
1,2,4-Trimethylbenzene	0.13
1,2,3-Trimethylbenzene	0.13

of sorption. Physical limitations to equilibrium include diffusion controlled adsorption-desorption processes (Rao and Davidson, 1979) or the presence of physical barriers limiting the interaction of the sorbent and solute (eg. soil aggregates, surface films). The kinetics of chemical reactions between the sorbent and solute may be limiting, thereby explaining the nonequilibrium in the column breakthrough curves. Multisite models have been proposed to account for sorption nonequilibrium (Rao et al., 1979). However, the physical and chemical processes are mathematically equivalent when written in non-dimensional form, thus the identification of the process responsible for the observed nonequilibria is not possible from breakthrough curve data.

Sorption nonequilibria are also a function of the flow velocity. The observed effect of increased flow velocity is displacement of the elution curve towards a smaller breakthrough volume, whereas the calculated effect of increased flow velocity is a broadening of the elution curve, owing to increased dispersion, without a change in the position of the position of the BTC. This effect was demonstrated by Schwarzenbach and Westall (1981) where retardation factors decreased with increased flow rates, indicating slow sorption kinetics.

Rao and Davidson (1979) illustrated that the retardation factor may also be a function of concentration, with increased concentration of solutes leading to decreased

sorption. This results from nonlinearity of the sorption isotherm, which governs the position of the breakthrough curve.

The BTC data in this study were obtained for a single flow velocity and at only one range of concentrations. However, the importance of increased flow velocity and high concentration on the transport of contaminants may be significant at the Lake Alfred field site. Killan (1987) reported seepage velocities of 1 to 18 feet per day in the Lake Alfred aquifer. This high flow velocity, combined with the high levels of hydrocarbon contamination and oxygen limitation in certain areas at the Lake Alfred site suggests that movement of solutes may be more rapid than these column experiments would predict. The sorption isotherms calculated in this study were based on linear isotherms, for concentrations which were present in the well water. However, it is possible that residual gasoline in the aquifer may provide higher concentrations in selected areas, leading to more rapid leaching of aromatic solutes owing to higher concentrations (eg., the sorption isotherms may be nonlinear, and R may be concentration dependent).

5.5.3 Comparison of Column and Equilibrium Isotherm Data.

Retardation factors (Table 5-11) and sorption coefficients (Tables 5-10 and 5-7) from the column data and the equilibrium data isotherm compare favorably. On average, K_d values from regression analysis of isotherm data using the linear model overestimate the value of the sorption coefficients by 40%, and the Freundlich model underestimates the value of the sorption coefficients by 33% relative to the column derived sorption coefficients.

Based on this comparison, the column data appear to fall within a range of values bounded by the batch isotherm data. In the following discussion, sorption coefficients from the column data are used to evaluate various sorption relationships. Column data are used here since they are equivalent to the isotherm data, and also since the column data provide values for ethylbenzene and the propylbenzenes which were not evaluated in the isotherm studies owing to low concentrations in the well water.

The retardation values of aromatic hydrocarbons in these experiments are relatively low. The retardation values from the column studies range between 1.36 and 2.40. These data indicate that the most retained solute will continue to move at 42% the rate of water movement. Thus solutes may be expected to move relatively rapidly through the site.

5.6 Evaluation of Sorption Models

The actual mechanisms through which sorption retards the movement of solutes are not well known. Various conceptual models are available to help describe these sorption process. These include the partitioning between organic matter on the aquifer matrix (Chiou et al., 1979, Karickhoff et al., 1979), interactions with the mineral surfaces (Sabljic, 1987), and solvophobic theory (Rao et al., 1985). To assess the significance of these models, sorption data from the column experiments were compared to several theoretical models. The column data were normalized to the organic carbon content of the Lake Alfred aquifer. These values of K_{oc} are shown in Table 5-10.

5.6.1 Relationship between K_{ow} and K_{oc}

Several authors cite the linearity of the sorption isotherms as evidence of the dominance of the partitioning mechanism (Chiou et al., 1979, Chiou et al., 1983). However this evidence may be suspect, if the range of concentrations is far removed from the maximum solubility of the compounds. In addition, many sorption models are indistinguishable over sufficiently small concentration ranges (Curtis et al., 1986). In this study, solute concentrations are far below the solubility limits. The least soluble compounds in this work are 3 ethyltoluene and 4-ethyltoluene with aqueous solubilities of 40 mg/L. However, the maximum concentration employed in this study is 935 ug/L, which is only 2% of the

maximum solubility level. Therefore, the fact that the isotherms are linear in this study does not confirm the dominance of the partitioning theory.

An improved method to assess the importance of partitioning in the sorption process at the Lake Alfred site is to compare K_{oc} values from this work with octanol-water partition coefficients (Figure 5-8) and water solubility (Figure 5-9) from the literature. The regression coefficients for these correlations are shown in Table 5-13. These experimentally derived relationships can now be compared with those from previous studies.

The experimentally derived relationships between K_{oc} and K_{ow}, and K_{oc} and WS were determined by regression of literature values of K_{ow} and water solubility with K_{oc} data from the sorption BTC data. These relationships are

$$\log K_{oc} = 0.31 * \log Kow + 1.91 \qquad [5.2]$$
$$\log K_{oc} = -0.272 * \log WS \text{ (umoles/L)} + 3.78 \qquad [5.3]$$

Table 5-14 compares the predicted values of K_{oc} from the work of several authors (Karickhoff et al., 1979, Means et al., 1982, Chiou et al., 1983, Kenaga and Goring, 1980, Briggs, 1981). The K_{oc} data from this study (Table 5-10) consistently fall within the upper range of the predicted values shown in Table 5-14. The relationships used to calculate the values in Table 5-14 were based on a wide range of organic solutes and natural sorbent materials. It
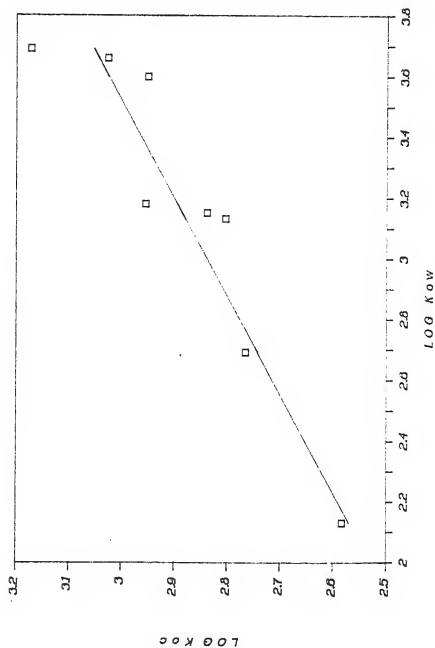
Figure 5-8. Log K_{oc} vs. log K_{ow} for study compounds.
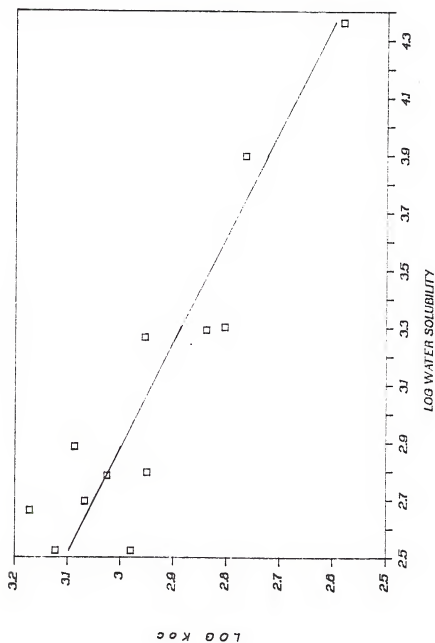
Figure 5-9. Log K_{OC} (from column data) vs. log WS for study compounds.

Table 5-13.   Regression coefficients for plots of log
K_{oc} vs. log K_{ow} and log K_{oc} vs. log WS.

Log K_{oc} vs. Log K_{ow}		Log K_{oc} vs. Log WS[a]	
Slope	0.310	Slope	-0.272
Std. error of slope	0.052	Std. error of slope	0.039
Y-intercept	1.909	Y-intercept	3.785
Std. error of y-intercept	0.073	Std. error of y-intercept	0.074
r^2	0.857	r^2	0.828
Number of observations	8	Number of observations	12
Degrees of freedom	6	Degrees of freedom	10

[a] umoles/L

Table 5-14. Comparison of relationships to predict K_{ow} from K_{ow} values.

Compound	log K_{ow}	log K_{oc} values from:					Range log K_{oc}
		Karickoff[a]	Means[b]	Chiou[c]	Kenaga[d]	Briggs	
Benzene (min.)	1.56	1.35	1.24	0.62	2.22	1.45	0.62-2.61
(max.)	2.28	2.07	1.96	1.27	2.61	1.83	
Toluene (min.)	2.11	1.90	1.79	1.12	2.52	1.74	1.12-2.85
(max.)	2.73	2.52	2.41	1.68	2.85	2.06	
Ethylbenzene	3.15	2.94	2.83	2.06	3.08	2.28	2.06-3.08
m,p-Xylene	3.18	2.97	2.86	2.08	3.10	2.29	2.08-3.10
o-Xylene (min.)	2.77	2.56	2.45	1.71	2.88	2.08	1.71-3.07
(max.)	3.13	2.92	2.81	2.04	3.07	2.27	
Isopropylbenzene	3.66	3.45	3.34	2.51	3.36	2.54	2.51-3.45
n-Propylbenzene (min.)	3.57	3.36	3.25	2.43	3.31	2.50	2.43-3.37
(max.)	3.68	3.47	3.36	2.53	3.37	2.55	
1,3,5-Trimethylbenzene (min.)	3.42	3.21	3.10	2.30	3.23	2.51	2.30-3.39
(max.)	3.60	3.39	3.28	2.46	3.32	2.51	
1,2,3-Trimethylbenzene	3.60	3.39	3.28	2.46	3.32	2.51	2.46-3.39

[a] Karickoff et al., 1979: log K_{oc} = 1.00 * log K_{ow} - 0.21

[b] Means et al., 1982: log K_{oc} = 1.00 * log K_{ow} - 0.32

[c] Chiou et al., 1983: log K_{oc} = 0.90 * log K_{ow} - 0.78

[d] Kenaga and Goring, 1980: log K_{oc} = 0.54 * log K_{ow} + 1.38

[e] Briggs, 1981: Log K_{oc} = 0.52 * log K_{ow} + 0.64

is notable that K_{oc} from this study falls in the upper range of the predicted K_{oc} values, given the paucity of organic carbon in the Lake Alfred aquifer material. A comparison of predicted K_{oc} values calculated from water solubility relationships of several authors and that of equation [5.3] also show that the experimental K_{oc} values from this study are generally in the upper range of these predicted values as well.

The relatively high values of K_{oc} predicted from equations [5.2] and [5.3] may be the result of several factors: 1) error in the measurement of organic carbon, 2) increased hydrophobicity of the organic matter at Lake Alfred compared to the referenced studies, 3) sorption to the mineral surface, or 4) any combination of the above (Curtis et al., 1986). It is unlikely that the organic matter in this study is more hydrophobic than that used by other researchers. This is confirmed by analysis of the slopes of the regression lines in the relationships between K_{oc} and K_{ow}. The slope of a plot of K_{oc} vs. K_{ow} may be viewed as a measure of the hydrophobicity of the organic phase in the partitioning model (Leo et al., 1971). In the experimental data presented here the slope of equation [5.2] was less than that observed in previous studies where partitioning is thought to predominate. This is presented graphically in Figure 5-10. Therefore, increased hydrophobicity of the organic matter at Lake Alfred was ruled out.
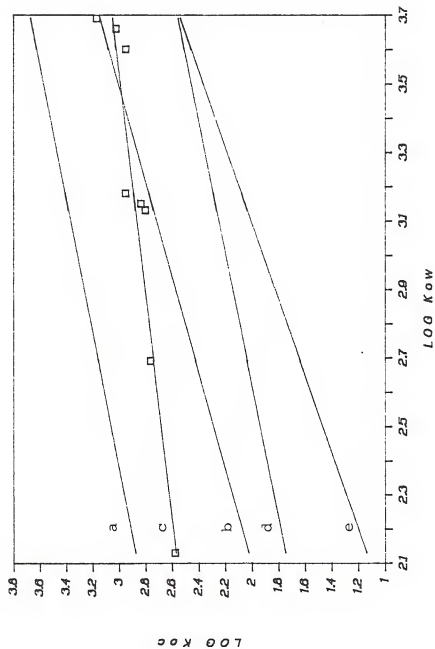
Figure 5-10. Regression equations for several models describing the relationship between K_{oc} and K_{ow}: (a) Curtis et al., 1985, (b) Schwarzenbach and Westall, 1981, (c) this study, (d) Briggs, 1981 and (e) Chiou et al., 1983.

It is more likely that the increased sorption results from some affinity of the aromatic solutes in this study for the mineral surface of the aquifer material. This is consistent with the findings of Schwarzenbach and Westall (1981) and Curtis et al., (1986). These authors demonstrate that the mineral surface area and the nature of the mineral surface, exert a greater influence on sorption than organic carbon for sorbents with low amounts of naturally occurring organic material.

5.6.2 <u>Relationship Between ^1X and K_{oc}</u>

To assess the contribution of the mineral surface in the sorption of aromatic solutes from the Lake Alfred aquifer, K_{oc} values from this study were correlated with first order molecular connectivity indices (^1X). This relationship is shown in Figure 5-11 and the regression parameters are shown in Table 5-15. The use of this correlation was based on the suggestion of Milgelgrin and Gerstl (1983) that molecular structure or topology may be more effectively correlated with sorption than K_{ow} or WS. Sabljic (1987) suggested the use of first order molecular connectivity indices (^1X) as an estimator of molecular topology. The regression equation developed by Sabljic (1987) is also shown in Figure 5-11. This relationship was based on the regression of calculated ^1X versus literature values of K_{oc} data.

The slopes of these lines are not significantly different at the 0.05 significance level. The correlation
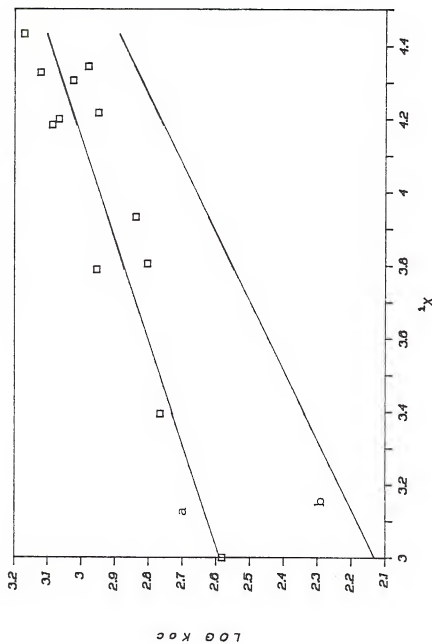
Figure 5-11. Log K_{oc} vs. $^1\chi$ for aromatic solutes in (a) this study and from (b) Sabljic (1987).

Table 5-15. Regression coefficients for the relationship between $\log K_{oc}$ and $^1\chi$.

Slope	0.360
Std. error of slope	0.050
Y-intercept	1.509
Std. error of y-intercept	0.072
r^2	0.839
Number of observations	12
Degrees of freedom	10

coefficients are also comparable: 0.916 for this study vs 0.976 for Sabljic (1987). Sabljic (1987) demonstrated that first order molecular connectivity was a quantitative measure of the area occupied by the projection of the non-hydrogen skeleton of a molecule. The goodness of fit between ^1X and K_{oc} data in this study supports the hypothesis that sorption depends, at least in part, on some type of surface interaction.

However, comparison of correlation coefficients between the three models (K_{ow}, WS and ^1X) indicates that neither of these models completely describe the sorption process (see Tables 5-13 and 5-15). This suggests that the sorption mechanism is in reality a combination of processes, interacting to yield an overall sorption effect. The lack of any dominant mechanism may be more pronounced in this study resulting from the low organic carbon content of the Lake Alfred aquifer material. This serves to reduce the partitioning effect, by eliminating the sorption substrate (organic carbon). In addition, Schwarzenbach and Westall (1981) demonstrated that organic poor sorbents with high specific surface areas may still exhibit small K_d values, indicating that surface interactions alone did not completely account for sorption. These data support the observation of Voice and Weber (1983) that, given the heterogeneous nature of natural sorbent materials, sorption mechanisms of organic solutes in the environment probably involve many types of interactions. The importance of a

given reaction mechanism depends on the nature of the sorbent surface. Partitioning is probably more important in soils with high organic carbon contents. The varying degrees of sorption in soils with low organic carbon contents reported by Milgelgrin and Gerstl (1984) reflect the variation in the ability of mineral surfaces to sorb organic compounds.

5.7 Comparison of Mixed Solute and Single Solute Retardation.

Nkedi-Kizza et al. (1987) demonstrated the influence of organic co-solvents on the movement of hydrophobic organic compounds through soils. In this dissertation, the study compounds were a multicomponent mixture of dissolved aromatic solutes, resulting from the partial solubilization of a leaded gasoline product into groundwater at the Lake Alfred site. The presence of multiple solutes may affect the sorption of a single component of the mixture either by changing the solubility of the component or through competitive sorption (Brookman et al., 1985). To evaluate this possibility, a single solute (benzene, 4 mg/L dissolved in RAP-2 well water) was passed through a soil column. The breakthrough of this solute is shown in Figure 5-12. Evaluation of the retardation factor for this column yielded an R value of 1.4, which is equivalent to the R value for benzene from the mixed solute sample. Based on these data, no co-solute effect on benzene was observed. If a
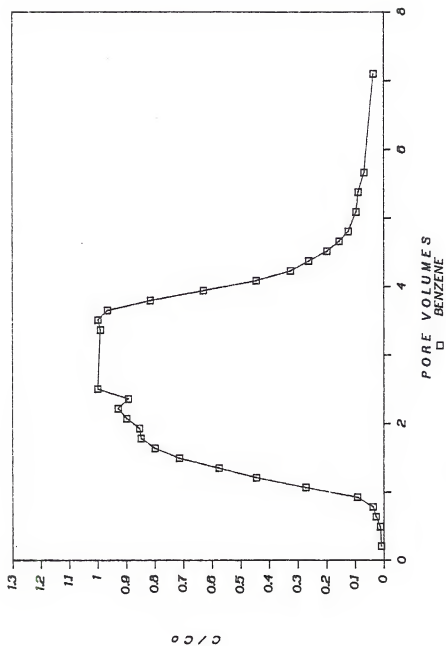
Figure 5-12. Breakthrough curve for benzene (single solute) spiked into RAP-2 well water ($C_o = 4000$ ug/L).

competitive sorption effect is operating in the mixed solute sample, then benzene as a single solute should show increased sorption. Lack of sorption increase indicates that competitive sorption between solutes was not important in this experimental system although this may not be the case in portions of the aquifer with residual concentrations of gasoline.

5.8 Evaluation of Hydrogen Peroxide Reactivity

Hydrogen peroxide is known to be a viable method of increasing the dissolved oxygen in aquifer systems (Britton, 1985, TRI Report, 1982). The purpose of this experiment was to evaluate the reaction kinetics and the extent of conversion of hydrogen peroxide to O_2 in the Lake Alfred aquifer system.

Initial experiments with distilled deionized water and known additions of dilute hydrogen peroxide showed no increases in dissolved oxygen. Even after addition of 5 mL of 50% hydrogen peroxide to the reaction flask, no increase in dissolved oxygen was noted over a 45 minute interval. The titer of the 50% stock solution (49.7%) was confirmed by titration with potassium permanganate. These data indicated the stability of hydrogen peroxide in the absence of a catalyst.

The reaction of hydrogen peroxide in filter sterilized Lake Alfred water was investigated to assess the

availability of non-biological catalysts in the aqueous phase. Water from wells OHM-4 (with aromatic solutes) and RAP-2 (no aromatic solutes) were titrated with hydrogen peroxide solutions of 240 and 2400 mg/L with no apparent increase in dissolved oxygen, indicating an the absence of a H_2O_2 active catalyst in both these water samples.

The response of non-filtered water from well OHM-4 to the addition of 50% hydrogen peroxide is shown in Figure 5-13. The pH of the water in the reaction flask was 6.5 and this value remained constant throughout the course of the experiment. The redox potential increased from 59 milli-volts (mv) to 338 mv immediately following the addition of 500 ul of 50% H_2O_2 (equivalent to 2000 mg/L H_2O_2). This addition of H_2O_2 was sufficient to maintain an increase of 1 mg/L over the ambient DO in the reaction flask. The addition of sterile aquifer material from the Lake Alfred site increased the DO of the reaction flask immediately after introduction. This indicated the catalytic ability of the Lake Alfred aquifer and was most likely associated with the presence of iron salts (Britton 1985) although iron concentrations were not determined for the Lake Alfred aquifer material. This small scale study helped to determine the reactivity of the hydrogen peroxide in the Lake Alfred aquifer system, and provided ranges for use of hydrogen peroxide in the biological experiments. Gas chromatographic analyses of aromatic compounds during the course of this experiment showed that there were no
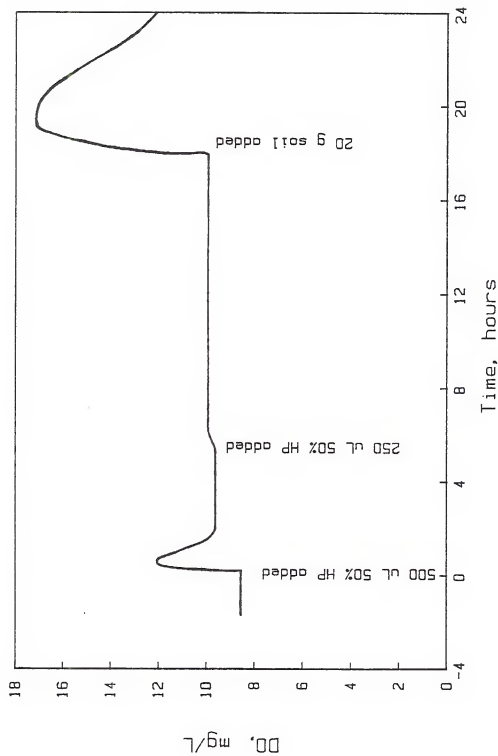
Figure 5-13.   Reaction of OHM-4 well water to the addition of 50% hydrogen peroxide and aquifer material.

measurable changes in the concentrations of these solutes resulting from the addition of hydrogen peroxide. The absence of aromatic hydrocarbon removal in this experiment should not imply that H_2O_2 is an ineffective method of oxygen augmentation. The dissolved oxygen levels did increase in this experiment. However, removal of hydrocarbons, abiotically, via oxidation of the aromatic molecules appeared not to be significant. This experiment was not designed to measure the microbial removal of hydrocarbons. The time scale of this experiment was too short to observe a microbial effect. Batch biodegradation experiments (sections 5.8 and 5.9) demonstrated that several days were required for microbial adaptation to hydrogen peroxide.

The data from this experiment simply confirm that there are sufficient catalysts available to mediate the conversion of H_2O_2 to O_2. Application of H_2O_2 to the Lake Alfred aquifer is underway. Preliminary data indicate that dissolved oxygen levels were increased, and that hydrocarbons concentrations were reduced following an adaptation period.

5.9 Batch Biodegradation Experiment #1

Two separate batch biodegradation experiments were performed. The first experiment was designed to investigate the effect of various combinations of hydrogen peroxide and

ammonium chloride on the biodegradation of the aromatic compounds in the Lake Alfred aquifer, and to assess the degradation of these compounds in the presence of dissolved oxygen. The average concentrations of aromatic hydrocarbons in the microcosms of experiment #1 over the time course of the experiment (31 days) are shown in Table 5-16. A detailed presentation and statistical analysis of these data are presented in Appendix E. These data were fit to several rate equations. Zero order, first order, an empirically based first order rate equation (Thomas-slope method), second order, and a mixed order (zero to first order) rate equations were fit to the biodegradation data. Only the first order rate equations gave adequate fit to the data, based on an analysis of the coefficients of determination for the various models (Global F-test, 0.05 significance level). The results of linear regression analysis of the data to the first order models are shown in Table 5-17 (first order) and Table 5-18 (Thomas-slope). In both tables the rate constants, calculated half lives and the coefficients of determination for each solute under each treatment condition are presented.

Regression analyses and rate data for both types of first order rate equations are presented, since neither method yields coefficients of determination which consistently provide superior fit to the data. First order and Thomas slope rate equations each provide adequate fit to the data as evidenced by the r^2 values. In the sections

Table 5-16. Total average hydrocarbon values (ug/L) in the microcosms of batch biodegradation experiment #1.

Compound	Day	1A	1B	1C	1D	1E	1F	1G
					Treatment			
Benzene	0	828.35	633.93	663.87	870.85	692.00	692.00	611.33
	3	107.85	668.83	508.87	588.83	666.00	476.33	393.00
	7	55.00	681.00	213.09	274.20	259.33	499.00	547.00
	15	0.00	222.95	8.93	168.27	93.33	473.50	464.33
	31	0.00	0.00	0.00	1.15	7.00	185.00	384.67
Toluene	0	2170.91	1735.47	1803.10	2141.95	1691.67	1691.67	1422.00
	3	53.45	1348.13	1070.47	1091.70	1509.33	105.67	780.67
	7	39.33	1416.30	192.68	144.45	151.00	388.00	1079.00
	15	13.65	414.50	35.53	224.20	74.00	191.00	907.00
	31	0.00	0.00	0.00	0.55	3.67	56.00	753.00
m,p-Xylene	0	4823.27	3548.30	3898.10	4664.55	3068.33	3068.33	3528.67
	3	1623.15	1608.97	1823.30	652.13	2013.67	2311.67	1984.33
	7	924.83	1826.93	53.35	18.20	33.00	40.00	2342.67
	15	40.65	935.95	57.30	83.13	29.00	25.25	1966.33
	31	0.00	8.07	0.00	1.73	5.00	9.00	1565.33
o-Xylene	0	2755.48	2111.07	2272.20	2770.90	2215.67	2215.67	2237.67
	3	1652.45	1714.50	1737.33	1744.60	1884.67	1428.67	1313.00
	7	742.00	2110.50	943.53	1675.25	1468.00	1387.33	1723.67
	15	48.25	856.45	123.93	1294.70	1063.00	1230.00	1317.33
	31	0.00	3.67	0.45	8.45	211.00	624.33	1104.33

Table 5-16. Continued.

Compound	Day				Treatment			
		1A	1B	1C	1D	1E	1F	1G
3,4-ET[a]	0	915.59	659.17	867.00	858.30	675.33	675.33	717.67
	3	264.60	346.40	319.73	249.63	410.00	383.33	353.67
	7	168.37	409.85	46.30	60.20	69.00	66.00	414.33
	15	14.60	182.20	15.80	41.90	20.67	47.75	312.33
	31	0.00	4.83	0.00	4.13	3.33	8.67	224.00
1,3,5-TMB[b]	0	389.89	269.07	378.90	347.75	280.00	280.00	320.67
	3	218.30	204.73	188.93	214.47	185.33	130.33	165.33
	7	136.93	223.50	128.40	153.50	134.67	122.67	189.33
	15	3.80	83.55	38.50	132.37	125.67	94.75	129.33
	31	0.00	3.23	17.65	99.70	45.67	56.00	104.33
2-ET[c]	0	410.43	241.47	317.90	299.50	256.33	256.33	285.33
	3	167.60	187.80	178.93	212.07	175.67	145.00	146.33
	7	131.70	215.75	145.95	179.05	151.67	147.67	172.00
	15	33.15	100.50	33.90	137.73	131.00	128.00	126.00
	31	0.00	10.83	3.60	54.05	30.33	68.33	101.00
1,2,4-TMB[d]	0	1334.60	1121.87	1103.30	1113.70	980.00	980.00	1046.33
	3	442.55	388.13	422.70	89.90	349.33	548.33	537.67
	7	189.60	364.70	7.58	4.75	5.33	7.33	618.33
	15	14.90	181.20	9.63	4.90	7.67	9.00	414.67
	31	0.00	2.10	0.85	1.70	3.33	2.33	335.67

Table 5-16. Continued.

Compound	Day	Treatment						
		1A	1B	1C	1D	1E	1F	1G
1,2,3-TMB[e]	0	560.37	493.07	518.50	493.60	436.00	436.00	479.33
	3	309.30	306.93	291.23	315.47	306.00	241.33	264.00
	7	200.80	361.85	271.25	283.50	243.00	230.00	310.67
	15	12.70	169.60	73.27	219.13	243.00	184.25	222.00
	31	0.00	9.60	8.50	155.45	75.67	130.67	194.67
DO[f]	0	7.30	9.03	10.40	8.90	10.20	10.20	8.63
	3	1.50	1.50	1.03	2.20	2.10	9.80	7.87
	7	1.80	2.10	2.63	5.20	4.13	2.80	8.20
	15	2.70	2.40	3.77	4.00	5.40	5.43	7.95
	31	4.10	2.40	3.60	5.20	5.47	6.57	7.80

[a] 3,4-Ethyltoluene

[b] 1,3,5-Trimethylbenzene

[c] 2-Ethyltoluene

[d] 1,2,4-Trimethylbenzene

[e] 1,2,3-Trimethylbenzene

[f] Dissolved oxygen, in mg/L

Table 5-17. Biodegradation rate constants, half-lives and correlation coefficients for the fit of biodegradation experiment #1 data to a first order rate equation.

Treatment		Benzene	Toluene	m,p-Xylene	o-Xylene	3,4-ET[a]
1A	k	0.233	0.219	0.295	0.282	0.235
	$t_{\frac{1}{2}}$	2.97	3.17	2.35	2.46	2.95
	r^2	0.779	0.844	0.993	0.995	0.989
1B	k	0.233	0.262	0.190	0.208	0.135
	$t_{\frac{1}{2}}$	2.97	2.65	3.65	3.33	4.47
	r^2	0.887	0.901	0.909	0.876	0.928
1C	k	0.242	0.261	0.271	0.284	0.227
	$t_{\frac{1}{2}}$	2.86	2.66	2.56	2.44	3.05
	r^2	0.970	0.994	0.913	0.975	0.967
1D	k	0.212	0.254	0.216	0.183	0.157
	$t_{\frac{1}{2}}$	3.27	2.73	3.21	2.79	4.42
	r^2	0.942	0.920	0.753	0.868	0.921
1E	k	0.154	0.200	0.200	0.076	0.171
	$t_{\frac{1}{2}}$	4.50	3.47	3.47	9.17	4.05
	r^2	0.992	0.952	0.753	0.969	0.936
1F	k	0.038	0.107	0.185	0.036	0.134
	$t_{\frac{1}{2}}$	18.3	6.48	3.75	19.47	5.17
	r^2	0.885	0.945	0.706	0.917	0.897
1G	k	0.010	0.013	0.020	0.017	0.030
	$t_{\frac{1}{2}}$	69.31	51.7	35.55	40.29	23.42
	r^2	0.370	0.401	0.625	0.584	0.724

Table 5-17. Continued.

Treatment		1,3,5-TMB[b]	2-ET[c]	1,2,4-TMB[d]	1,2,3-TMB[e]	DO[f]
1A	k	0.223	0.207	0.249	0.230	
	$t\frac{1}{2}$	3.11	3.35	2.78	3.01	
	r^2	0.935	0.982	0.989	0.986	0.013
1B	k	0.145	0.102	0.193	0.126	
	$t\frac{1}{2}$	4.78	6.80	3.59	5.50	
	r^2	0.936	0.937	0.939	0.933	0.093
1C	k	0.097	0.146	0.214	0.133	
	$t\frac{1}{2}$	7.17	4.75	3.24	5.21	
	r^2	0.927	0.994	0.777	0.990	0.111
1D	k	0.034	0.052	0.172	0.033	
	$t\frac{1}{2}$	20.21	13.30	4.03	21.00	
	r^2	0.775	0.982	0.632	0.875	0.0
1E	k	0.053	0.065	0.164	0.052	
	$t\frac{1}{2}$	13.05	10.75	4.23	13.46	
	r^2	0.946	0.946	0.591	0.931	0.005
1F	k	0.043	0.036	0.183	0.032	
	$t\frac{1}{2}$	16.16	19.42	3.79	21.66	
	r^2	0.820	0.868	0.673	0.799	0.042
1G	k	0.030	0.026	0.030	0.023	
	$t\frac{1}{2}$	23.50	26.36	23.11	30.27	
	r^2	0.725	0.683	0.728	0.655	0.429

[a] 3,4-Ethyltoluene

[b] 1,3,5-Trimethylbenzene

[c] 2-Ethyltoluene

[d] 1,2,4-Trimethylbenzene

[e] 1,2,3-Trimethylbenzene

[f] Dissolved oxygen

Table 5-18. Biodegradation rate constants, half-lives and
correlation coefficients for the fit of
biodegradation experiment #1 data to the
Thomas slope rate equation.

Treatment		Benzene	Toluene	m,p-Xylene	o-Xylene	3,4-ET
1A	k^a	0.224	0.239	0.188	0.139	0.195
	$t_{\frac{1}{2}}^b$	3.09	2.91	3.68	4.97	3.56
	r^2	0.964	0.958	0.974	0.999	0.967
1B	k	-3.406	-0.155	0.135	-0.155	0.111
	$t_{\frac{1}{2}}$	-0.204	-4.46	5.14	-0.107	6.27
	r^2	0.764	0.129	0.838	0.129	0.745
1C	k	0.094	0.153	0.183	0.087	0.195
	$t_{\frac{1}{2}}$	7.37	4.54	3.79	7.93	3.55
	r^2	0.899	0.986	0.987	0.947	0.984
1D	k	0.118	0.171	0.228	0.096	0.205
	$t_{\frac{1}{2}}$	5.90	4.06	3.04	7.21	3.38
	r^2	0.978	0.975	0.966	0.712	0.972
1E	k	-0.027	0.048	0.144	0.045	0.151
	$t_{\frac{1}{2}}$	-25.99	14.30	4.80	15.33	4.60
	r^2	0.040	0.199	0.946	0.926	0.982
1F	k	0.101	0.142	0.116	0.130	0.160
	$t_{\frac{1}{2}}$	6.88	4.89	5.96	5.31	4.33
	r^2	0.568	0.989	0.822	0.816	0.983
1G	k	0.130	0.177	0.176	0.157	0.173
	$t_{\frac{1}{2}}$	5.33	3.92	3.93	4.41	4.00
	r^2	0.488	0.780	0.863	0.761	0.883

Table 5-18. Continued.

Treatment		1,3,5-TMB	2-ET	1,2,4-TMB	1,2,3-TMB	DO
1A	k	0.140	0.165	0.193	0.140	0.382
	$t_{1/2}$	4.96	4.20	3.59	4.94	1.81
	r^2	0.988	0.955	0.978	0.984	0.990
1B	k	0.032	0.012	0.172	0.078	0.259
	$t_{1/2}$	21.66	56.98	4.04	8.85	2.68
	r^2	0.139	0.012	0.925	0.526	0.952
1C	k	0.158	0.129	0.197	0.122	0.262
	$t_{1/2}$	4.39	5.38	3.52	5.70	2.64
	r^2	0.975	0.949	0.986	0.903	0.955
1D	k	0.166	0.106	0.235	0.148	0.310
	$t_{1/2}$	4.17	6.57	2.96	4.67	2.24
	r^2	0.969	0.889	0.964	0.933	0.939
1E	k	0.127	0.102	0.210	0.110	0.324
	$t_{1/2}$	5.45	6.81	3.44	6.30	2.14
	r^2	0.896	0.786	0.985	0.785	0.940
1F	k	0.176	0.151	0.167	0.169	0.074
	$t_{1/2}$	3.95	4.60	4.15	4.10	9.37
	r^2	0.924	0.850	0.981	0.923	0.183
1G	k	0.171	0.176	0.170	0.174	0.176
	$t_{1/2}$	4.05	3.95	4.07	4.00	3.94
	r^2	0.897	0.890	0.896	0.885	0.801

[a] day^{-1}

[b] days

below, each treatment is discussed individually, prior to an overall analysis of these experiments.

5.9.1 Treatment 1A.

Data are plotted in Figures 5-14 and 5-15. The dissolved oxygen in these microcosms was not artificially increased, other than by aeration during the transfer and filling of the solute containing water into the biodegradation vials. The DO of these vials at time = 0 was 7.3 mg/L. An examination of the half lives of these solutes showed that benzene (3.1 days) and toluene (2.9 days) were readily removed from the microcosm compared to a half life of 4.96 for 1,3,5-trimethylbenzene. This is in contradiction to studies which note the recalcitrance of these compounds to biodegradation (Bossert and Bartha, 1984). The ortho isomer of xylene was more resistant to microbial attack than were the meta and para isomers. This confirmed the data of Kappeler and Wuhrmann (1978a, 1978b). Complete degradation of all solutes was achieved by 31 days (detection limit 0.5 ug/L) and in many cases degradation was complete in 15 days. Toluene was degraded particularly rapidly. The depletion of oxygen in these microcosms suggested that this loss was microbially mediated (Figure 5-16).

5.9.2 Treatment 1B.

Data for this treatment are shown in Appendix E . These data demonstrate the effect of 17 mg/L hydrogen peroxide treatment on the degradation of the aromatic

121
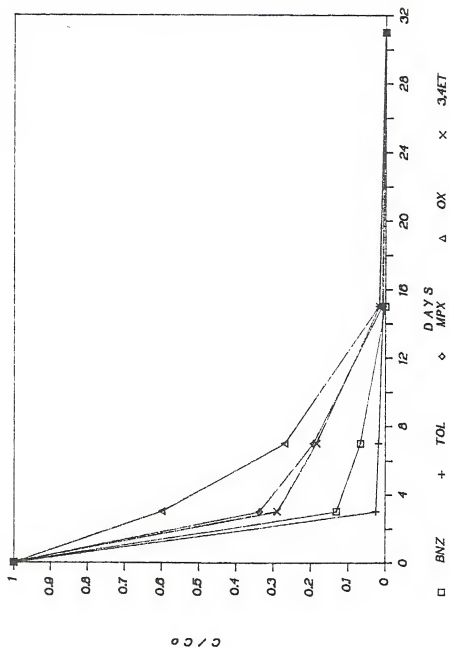
Figure 5-14. Relative concentration vs. time for five aromatic compounds in biodegradation treatment 1A.
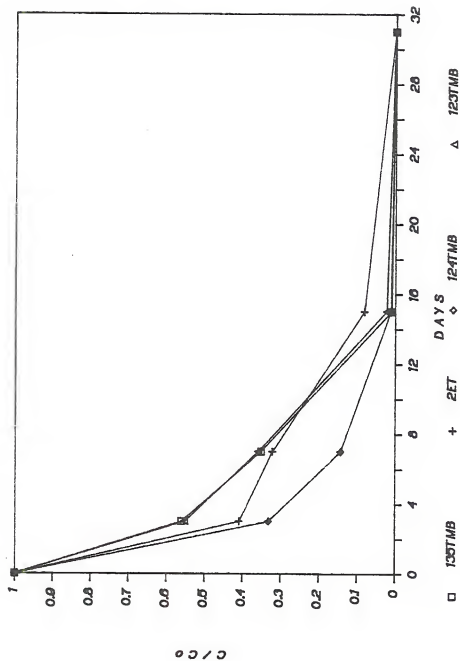
Figure 5-15. Relative concentration vs. time for four C_9H_{12} compounds
in biodegradation treatment 1A.

solutes. The main feature of these plots is the eight day lag phase in the removal of benzene, toluene and o-xylene. However, with time, degradation of these compounds was essentially complete. The C_9H_{12} compounds also displayed a lag up to eight days in length. The half lives were slightly increased over treatment 1A, indicating the time involved in the adaption of the microorganisms to the hydrogen peroxide.

5.9.3 Treatment 1C

The effects of increasing the concentration of H_2O_2 to 68 mg/L was shown in this treatment. There was no apparent increase in toxicity over the 17 mg/L treatment. Benzene, toluene and m,p-xylene were completely removed. Again, 1,2,4-trimethylbenzene exhibited the most rapid degradation of the C_9H_{12} compounds. The initial DO in these microcosms was 10.5 mg/L. The increased half lives of the study compounds reflect the adaptation to hydrogen peroxide noted in treatment 2B. Dissolved oxygen concentrations are shown in Figure 5-16.

5.9.4 Treatment 1D

Ammonium chloride (18mg/L) was added to these vials. This concentration was chosen based on the calculated amount of nitrogen required to completely degrade the aromatic solutes assuming a C:N ratio of 10:1. The initial DO concentration was 9 mg/L. Oxygen consumption appeared rapid but fell after seven days. Addition of ammonium chloride significantly reduced the rate of microbial degradation of

124
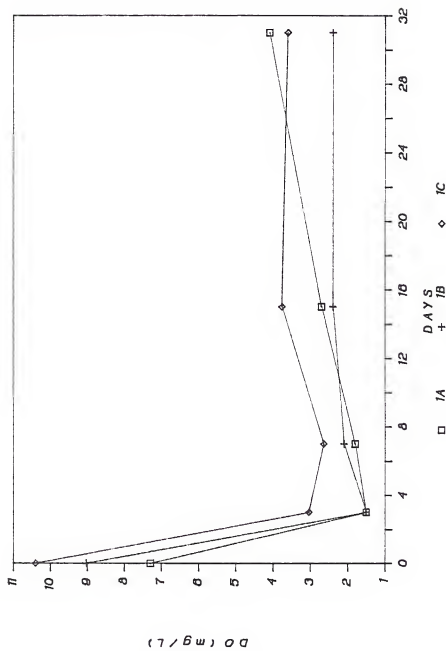
Figure 5-16. Concentration vs. time for dissolved oxygen in biodegradation treatments 1A, 1B and 1C.

benzene, toluene, 1,3,5-trimethylbenzene, 2-ethyltoluene,
and 1,2,3-trimethylbenzene. Both m,p-xylene (half life = 3
days) and 1,2,4-trimethylbenzene (half life = 2.96 days)
were less affected and were each degraded to 1.7 ug/L. At
the end of 31 days, 31% of 1,2,3-trimethylbenzene remained
but 1,3,5-trimethylbenzene, 2-ethyltoluene and 1,2,4-
trimethylbenzene although not completely degraded were well
removed.

5.9.5 Treatment 1E

Graphical representation of this treatment is shown in
Appendix E. These vials are treated with 18 mg/L NH_4Cl and
17 mg/L H_2O_2. This combination of treatments caused an
increase in the 1/2 lives for the C_6-C_8 compounds, but the
removal rates of the C_9H_{12} compounds were improved relative
to treatment with ammonium chloride alone. Ultimate removal
of compounds was good except for the more recalcitrant o-
xylene, 1,2,3-trimethylbenzene, 3,4-ET and 1,3,5-
trimethylbenzene. The lag in degradation of the aromatic
solutes was reflected in the reduced consumption of DO in
the microcosms (Figure 5-17).

5.9.6 Treatment 1F

Treatment with 68 mg/L H_2O_2 and 18 mg/L NH_4Cl is shown
in Appendix E and average data are shown in Table 5-16.
There was an obvious lag in the DO profile (Figure 5-17),
and the half life for dissolved oxygen was increased from
1.8 days in treatment 1A to 9.4 days in this treatment.
This was also reflected in the concentrations of benzene, o-
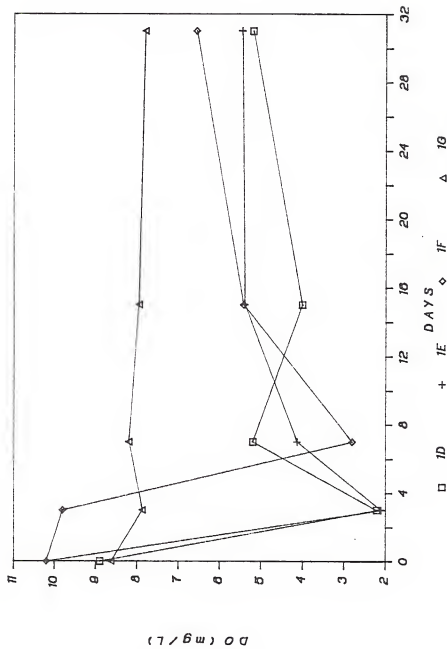
Figure 5-17. Concentration vs. time for dissolved oxygen in biodegradation treatments 1D, 1E, 1F and 1G.

xylene, 2-ethyltoluene, 1,3,5-trimethylbenzene and 1,2,3-trimethylbenzene. All compounds showed a substantial increase in half lives, except for m,p-xylene and 1,2,4-trimethylbenzene. Throughout this study these compounds were well degraded. These compounds were the most rapidly removed compounds in the work of Kappeler and Wuhrmann (1978a, 1987b). The changes in the degradation rates for the other aromatic compounds may reflect a change in the community structure of the well water bacteria. The bacteria from the field site may be adapted to degrade aromatic compounds that are usually thought to be recalcitrant or degraded slowly (i.e., benzene). In treatment 1A, benzene was rapidly and easily removed by the bacterial community. However, by disrupting this community by the addition of additional nutrients and hydrogen peroxide, only the compounds which are more easily biodegraded are removed. It may be possible that if these experiments were carried out for longer incubation periods, the microbial communities may have adapted to efficiently degrade the remaining aromatic compounds.

5.9.7 <u>Treatment 1G</u>

This treatment was a sterile control. The DO in this system remained at the initial levels (Figure 5-17), indicating the sterility of the system. Losses from the system are in the range of 25-50% for C_6-C_8 solutes, and 55-65% for C_9H_{12} solutes. These losses were most likely the result of diffusion of the volatile components through the

teflon septa. The loss of volatile compounds was exacerbated by storage at 20 C. However, this does not account for the increased reduction of C_9H_{12} concentrations relative to the more volatile C_6-C_8. C_6-C_8 values would normally exhibit greater volatile losses. The biodegradation data were not corrected for these losses.

5.10 Batch Biodegradation Experiment #2

The second series of batch biodegradation experiments were performed to assess the efficacy of several methods of oxygen addition to the Lake Alfred aquifer, and to repeat some of the previous treatments. In this series of experiments, additional sterile controls were added to better assess the losses exhibited in biodegradation experiment #1 (treatment 1F). In addition, microbial activity was measured by quantifying the microbial reduction of INT to INT-formazan.

The data from this experiment were fit to several rate models as described in section 5.9. No single model gave a consistently good fit to the data. Mixed order (zero order to first order) and zero order rate equations did not match the data well as evidenced by low coefficients of determination.

Average values of hydrocarbons in the microcosms are shown in Table 5-19. Rate constants, and regression coefficients for the fit of biodegradation #2 data to the

Table 5-19. Total average hydrocarbon values (ug/L) in the microcosms of batch biodegradation experiment #2.

Compound	Day	Treatment								
		2A	2B	2C	2D	2E	2F	2G	2H	2I
Benzene	0	1392.25	1392.25	1392.25	1392.25	1392.25	1392.25	220.00	220.00	220.00
	3	128.17	835.33	986.00	750.67	649.40	652.33	2.00	170.00	148.00
	7	156.33	654.33	663.33	492.93	655.00	571.67	2.00	77.00	174.50
	14	138.70	492.00	865.33	141.97	731.33	735.67	2.05	19.50	158.00
	21	145.00	487.67	754.67	287.50	884.67	890.33	2.00	34.50	175.50
	35	73.00	133.67	743.33	181.00	755.33	647.00	2.50	24.50	144.33
Toluene	0	7758.50	7758.50	7758.50	7758.50	7758.50	7758.50	414.33	414.33	414.33
	3	197.33	4275.33	5069.00	3966.67	3299.50	3335.67	1.73	133.67	244.00
	7	353.00	2675.00	3435.00	2466.33	3245.67	2871.33	7.87	49.67	329.00
	14	240.50	1293.50	4399.00	704.33	3118.00	3537.00	29.48	16.00	222.00
	21	235.00	1287.33	3855.33	538.33	4287.33	4407.67	1.60	34.00	229.50
	35	81.00	174.67	3374.00	398.00	2637.00	3083.00	13.50	16.00	195.33
Ethbz	0	218.50	218.50	218.50	218.50	218.50	218.50	101.50	101.50	101.50
	3	24.77	78.00	86.50	112.57	44.00	31.00	0.00	0.00	10.00
	7	5.00	52.37	54.67	38.80	41.67	24.07	0.00	0.90	5.12
	14	9.40	28.10	78.67	14.65	35.33	33.33	3.78	0.55	4.00
	21	1.95	28.60	63.00	11.95	60.67	43.33	0.00	0.65	4.00
	35	8.37	7.13	56.47	5.50	47.33	29.00	0.00	1.00	5.30

Table 5-19. Continued.

Compound	Day	2A	2B	2C	2D	2E	2F	2G	2H	2I
						Treatment				
m,p-Xylene	0	7241.75	7241.75	7241.75	7241.75	7241.75	7241.75	1573.67	1573.67	1573.67
	3	973.67	3245.00	4153.33	3448.00	2542.50	3010.00	5.17	112.93	824.50
	7	1415.33	1561.00	2815.67	1905.17	2504.33	2456.67	17.27	7.50	859.50
	14	989.00	662.50	3405.00	555.00	2312.67	2872.33	54.15	11.45	762.50
	21	1030.00	704.93	3144.67	135.33	3368.00	3653.33	16.10	28.00	756.50
	35	420.67	63.33	2602.33	486.5	1626.67	2519.50	5.93	10.00	652.67
o-Xylene	0	3452.75	3452.75	3452.75	3452.75	3452.75	3452.75	1121.33	1121.33	1121.33
	3	1629.33	1835.00	2259.33	1848.33	1407.50	1640.00	23.97	754.33	655.50
	7	1076.67	1192.00	1555.67	1313.00	1396.00	1346.67	59.70	144.00	717.00
	14	674.00	870.00	2001.00	416.00	1326.67	1611.67	70.28	41.25	604.00
	21	605.00	810.33	1794.33	588.67	1899.33	2078.00	59.77	24.00	622.50
	35	241.67	102.33	1500.00	346.50	1397.33	1461.00	13.57	74.00	532.00
3,4-ET	0	1651.00	1651.00	1651.00	1651.00	1651.00	1651.00	462.67	462.67	462.67
	3	299.67	588.00	771.00	769.33	437.50	587.33	6.75	54.67	144.00
	7	307.67	327.33	524.33	336.67	412.00	450.00	7.30	5.70	144.00
	14	200.00	157.00	642.33	95.67	331.00	483.00	12.55	3.35	119.50
	21	236.33	163.67	575.67	46.00	561.00	627.00	5.90	8.00	111.50
	35	110.00	18.67	454.67	93.00	295.33	427.50	1.77	6.00	99.67
1,3,5-TMB	0	593.50	593.50	593.50	593.50	593.50	593.50	174.33	174.33	174.33
	3	261.00	215.00	285.67	277.33	156.50	217.33	48.75	79.67	58.50
	7	155.33	125.33	192.67	160.00	153.67	160.00	3.17	6.90	57.50
	14	91.50	100.50	250.67	79.00	143.00	182.33	9.38	12.00	53.00
	21	105.67	99.33	223.33	72.33	217.67	241.00	13.47	12.50	52.00
	35	54.00	11.00	179.33	47.00	154.33	168.00	1.87	8.50	44.33

Table 5-19. Continued.

Compound	Day	2A	2B	2C	2D	2E	2F	2G	2H	2I
2-ET	0	482.25	482.25	482.25	482.25	482.25	482.25	199.67	199.67	199.67
	3	238.33	200.00	260.67	269.33	148.00	199.33	24.87	85.00	67.50
	7	132.67	126.67	176.00	164.67	145.33	147.00	14.57	28.67	82.50
	14	100.00	108.00	225.33	64.00	137.33	170.67	18.58	11.00	63.00
	21	88.67	104.67	205.67	72.67	202.00	231.00	11.43	16.00	57.50
	35	47.33	16.33	165.67	49.00	144.33	157.00	9.47	12.50	51.00
1,2,4-TMB	0	2169.00	2169.00	2169.00	2169.00	2169.00	2169.00	657.67	657.67	657.67
	3	260.00	753.00	1042.33	952.67	549.50	818.33	1.33	22.67	257.00
	7	369.00	295.00	695.33	439.33	554.33	592.67	7.83	1.77	254.00
	14	164.50	114.00	898.00	106.00	510.67	653.67	15.33	3.15	233.00
	21	255.00	133.67	801.00	19.67	776.00	896.67	7.93	7.50	231.00
	35	110.67	10.00	639.67	109.50	346.00	610.00	1.70	4.00	199.00
1,2,3-TMB	0	812.00	812.00	812.00	812.00	812.00	812.00	364.00	364.00	364.00
	3	301.67	337.00	422.33	292.10	240.50	292.00	39.73	195.67	152.00
	7	243.67	222.67	301.67	282.33	247.67	262.67	24.27	46.00	156.00
	14	164.50	182.50	383.33	129.33	232.67	290.00	22.50	28.00	137.00
	21	148.00	192.00	362.00	139.67	332.00	405.67	23.10	49.50	137.50
	35	75.67	27.67	278.33	86.50	241.67	267.00	5.60	30.50	120.67
DO[a]	0	7.50	7.50	7.50	7.50	7.50	7.50	20.00	20.00	20.00
	3	2.73	2.43	7.43	8.53	8.08	8.53	4.45	6.40	9.60
	7	2.27	2.27	7.53	2.90	4.63	8.23	4.10	5.07	8.60
	14	3.53	2.90	7.80	3.73	5.37	7.73	3.23	-	7.35
	21	2.83	3.17	7.73	3.27	5.50	7.50	3.13	5.05	7.90
	35	1.93	3.33	7.27	1.85	3.27	6.95	3.47	2.95	6.30

[a] dissolved oxygen in mg/L

first order model are shown in Table 5-20 and via the Thomas slope method in Table 5-21. Examination of correlation coefficients from the fit of the Thomas slope model to the data in this experiment suggest that rate constants from this model selectively give an adequate estimate of the biological degradation constant.

5.10.1 Treatment 2A

This is a repeat of treatment 1A. The general trends were the same and the rate constants were equivalent. Again m,p-xylene and 1,2,4-trimethylbenzene showed rapid loss as noted in treatment 1A. The extent of degradation was not as complete as in treatment 1A. This may be the result of the increased concentration of toluene (7759 ug/L vs 2171 ug/L) and the concentration of m,p-xylene (7241 ug/L vs 4823 ug/L in 1A). There was a rapid loss in DO over the first two days, indicating microbial activity.

5.10.2 Treatment 2B

This is a repeat of treatment 1D. The half lives were generally higher, reflecting a decrease in hydrocarbon removal. There was a pronounced lag phase of 8 days for benzene (Figure 5-18). The lag in degradation for toluene, o-xylene, m,p-xylene and 2-ethyltoluene was two days. The DO profile in this treatment was consistent with that of 2A indicating O_2 removal during the first several days. However, microbial activity was increased over treatment 2A. This microbial activity did not result in significant degradation of hydrocarbons.

Table 5-20. Biodegradation rate constants and correlation
            coefficients for the fit of biodegradation
            experiment #2 data to a first order rate
            equation.

Treatment		Benzene	Toluene	Ethbz[a]	m,p-Xylene	o-Xylene
2A	k_2[b]	0.042	0.071	0.070	0.046	0.052
	r^2	0.462	0.486	0.344	0.618	0.972
2B	k_2	0.049	0.089	0.082	0.114	0.070
	r^2	0.887	0.942	0.919	0.955	0.894
2C	k_2	0.003	0.006	0.013	0.013	0.007
	r^2	0.105	0.317	0.619	0.619	0.403
2D	k_2	0.043	0.073	0.096	0.138	0.046
	r^2	0.621	0.877	0.884	0.986	0.800
2E	k_2	-0.004	0.006	0.017	0.017	0.002
	r^2	0.169	0.219	0.138	0.009	0.038
2F	k_2	-0.001	0.001	0.024	0.007	0.002
	r^2	0.003	0.012	0.177	0.179	0.029
2G	k_2	0.067	0.036	0.004	0.081	0.057
	r^2	0.234	0.057	0.002	0.266	0.406
2H	k_2	0.059	0.072	0.135	0.095	0.057
	r^2	0.640	0.683	0.469	0.398	0.500
2I	k_2	-0.002	0.007	0.049	0.010	0.004
	r^2	0.056	0.211	0.160	0.873	0.740

Table 5-20. Continued

Treatment		3,4-ET	1,3,5-TMB	2-ET	1,2,4-TMB	1,2,3-TMB
2A	k_2	0.046	0.049	0.048	0.049	0.048
	r^2	0.698	0.867	0.917	0.574	0.923
2B	k_2	0.105	0.086	0.073	0.130	0.072
	r^2	0.951	0.889	0.886	0.949	0.871
2C	k_2	0.017	0.015	0.013	0.016	0.012
	r^2	0.653	0.553	0.557	0.572	0.539
2D	k_2	0.078	0.057	0.053	0.091	0.045
	r^2	0.691	0.885	0.833	0.586	0.858
2E	k_2	0.019	0.010	0.008	0.022	0.008
	r^2	0.360	0.139	0.136	0.404	0.128
2F	k_2	0.013	0.011	0.009	0.012	0.006
	r^2	0.333	0.240	0.192	0.256	0.110
2G	k_2	0.103	0.096	0.058	0.085	0.085
	r^2	0.531	0.585	0.578	0.255	0.763
2H	k_2	0.091	0.070	0.067	0.087	0.056
	r^2	0.421	0.529	0.649	0.297	0.572
2I	k_2	0.024	0.018	0.021	0.016	0.014
	r^2	0.627	0.560	0.627	0.614	0.651

[a]Ethylbenzene

[b]day^{-1}

Table 5-21. Biodegradation rate constants and correlation coefficients for the fit of biodegradation experiment #2 data to the Thomas slope rate equation.

Treatment		Benzene	Toluene	Ethbz	m,p-Xylene	o-Xylene
2A	k^a	0.239	0.248	0.250	0.222	0.096
	r^2	0.915	0.929	0.948	0.893	0.962
2B	k	0.004	0.081	0.194	0.133	0.028
	r^2	0.020	0.902	0.921	0.971	0.373
2C	k	0.379	0.139	0.232	0.122	0.139
	r^2	0.850	0.384	0.920	0.802	0.466
2D	k	0.032	-0.016	0.170	0.124	0.031
	r^2	0.196	0.026	0.975	0.997	0.249
2E	k	0.597	0.153	0.256	0.201	0.298
	r^2	0.979	0.832	0.931	0.687	0.388
2F	k	0.228	0.212	0.249	0.237	0.212
	r^2	0.631	0.730	0.923	0.740	0.880
2G	k	0.230	0.232	–	0.227	0.215
	r^2	0.948	0.935	–	0.938	0.908
2H	k	0.098	0.174	0.174	0.246	0.158
	r^2	0.883	0.974	0.977	0.937	0.960
2I	k	–	–	0.287	0.123	–
	r^2	–	–	0.957	0.651	–

Table 5-21. Continued.

Treatment		3,4-ET	1,3,5-TMB	2-ET	1,2,4-TMB	1,2,3-TMB
2A	k	0.216	0.152	0.130	0.228	0.162
	r^2	0.909	0.960	0.961	0.914	0.915
2B	k	0.156	0.161	0.144	0.172	0.138
	r^2	0.942	0.890	0.863	0.961	0.843
2C	k	0.162	0.177	0.154	0.173	0.157
	r^2	0.858	0.850	0.813	0.852	0.754
2D	k	0.116	0.129	0.079	0.140	0.153
	r^2	0.987	0.986	0.910	0.999	0.880
2E	k	0.223	0.255	0.254	0.216	0.255
	r^2	0.832	0.881	0.858	0.801	0.856
2F	k	0.222	0.234	0.235	0.230	0.254
	r^2	0.852	0.859	0.786	0.846	0.704
2G	k	0.225	0.177	0.211	0.227	0.206
	r^2	0.940	0.961	0.943	0.940	0.935
2H	k	0.240	0.149	0.165	0.251	0.096
	r^2	0.946	0.968	0.989	0.934	0.718
2I	k	0.211	0.217	0.193	0.206	0.195
	r^2	0.905	0.898	0.841	0.886	0.871

[a] day^{-1}
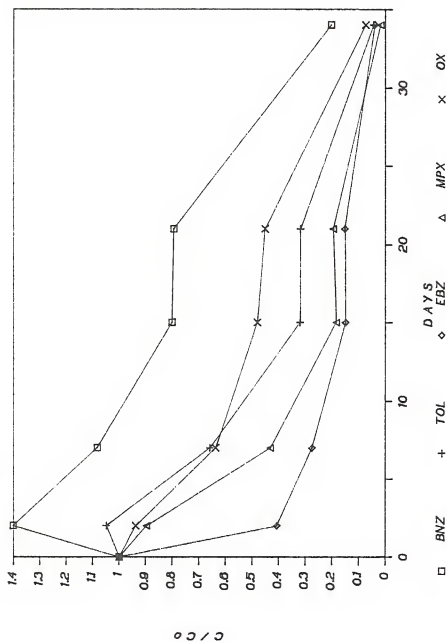
Figure 5-18. Relative concentrations of C_6-C_8 aromatic hydrocarbons vs. time in biodegradation treatment 2B.

5.10.3 Treatments 2D and 2E

These data assessed the effect of H_2O_2 addition on the microbial community. These were essentially repeats of treatments 1C and 1F. The addition of 58 mg/L H_2O_2 (treatment 2D) produced a 2 day lag phase for benzene, toluene, m,p-xylene and 2-ethyltoluene relative to no H_2O_2 treatment (Figure 5-19). The extent of treatment was comparable to treatment 2A (air addition). The DO profiles are shown in Figure 5-20. The lag in bioactivity was paralleled by a lag in consumption of DO for the same 2 day period. The addition of NH_4Cl in treatment 2E produced a toxic effect, and the hydrocarbon data were equivalent to the sterile control losses. However, the DO profile (Figure 5-20) showed consumption of dissolved oxygen, and this implied some microbial activity. The INT data also demonstrated increased bioactivity (Figure 5-21) following a lag of at least two days. Microbial activity decreased after 14 days. This decreased INT reduction was not noted for treatment 2D. Again, there was microbial activity and O_2 consumption without substantial reduction in hydrocarbon concentrations.

5.10.4 Treatments 2G, 2H, 2I.

These treatments showed the effect of the addition of oxygen gas to the microcosms. One consequence of the oxygen sparging was to reduce the initial concentrations of hydrocarbons from a total of 26,000 ug/L to 5000 ug/L. Benzene and toluene are preferentially removed, owing to
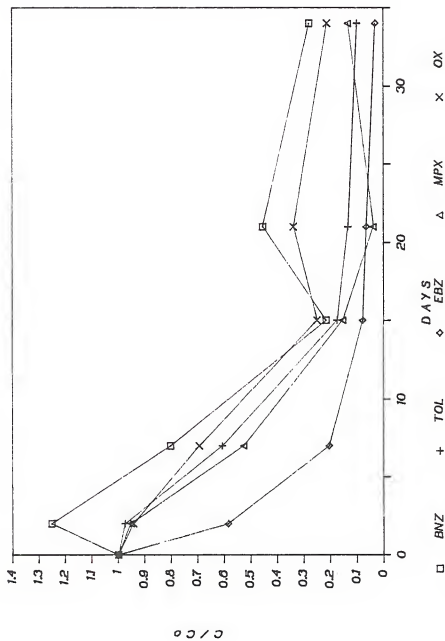
Figure 5-19. Relative concentrations of C_6-C_8 aromatic hydrocarbons vs. time in biodegradation treatment 2D.
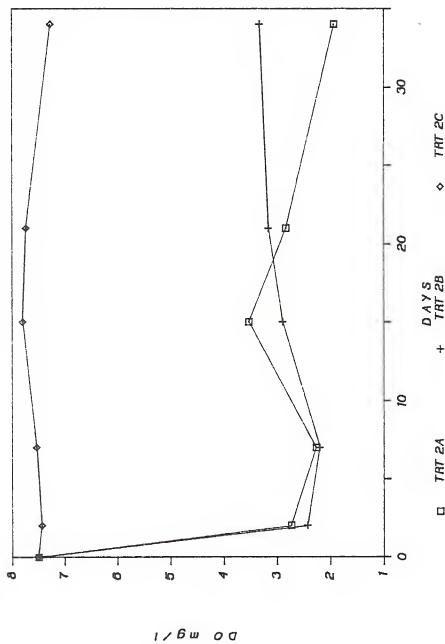
Figure 5-20. Concentration vs. time for dissolved oxygen in biodegradation treatments 2A, 2B and 2C.
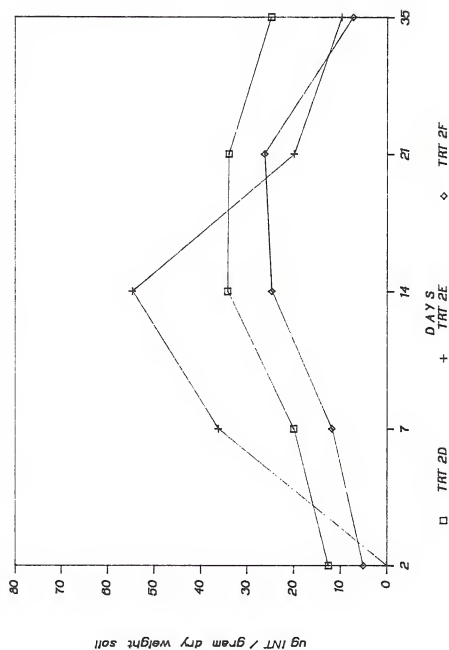
Figure 5-21. Electron transport activity in biodegradation treatments 2D, 2E and 2F.

their higher vapor pressure (95 torr for benzene and 29 torr for toluene compared with 6 torr for m-xylene at 25 C). The half lives for biodegradation under these conditions were in the same range as those for the higher concentrations (i.e. treatment 2A). Degradation to the low ug/L level was noted for all compounds. The most recalcitrant was o-xylene. The addition of NH_4Cl produced the same effect noted in other treatments. The lag phase seemed to be especially significant for benzene, o-xylene, 1,3,5-trimethylbenzene, 2-ethyltoluene and 1,2,3-trimethylbenzene. As in previous experiments, 1,2,4-trimethylbenzene was well degraded under all non-sterile conditions. The reduced treatment of solutes in 2H was accompanied by consumption of oxygen and an apparent increase in microbial activity. The DO profiles show that the concentration of dissolved oxygen remained above 4 mg/L throughout the entire study, indicating no oxygen limitation.

5.10.5 Treatments 2C, 2F, 2I (Sterile Controls)

Sterility in treatments 2C, 2F and 2G was indicated by the lack of O_2 consumption, low INT reduction and the persistence of aromatic hydrocarbons. The losses (assumed to result from diffusion through the teflon septa) were in the range of 0-25% for C_6-C_8 hydrocarbons and 20-50% for C_9H_{12} compounds. Sorption losses were accounted for in these data by adding the amount lost to sorption to the aqueous concentration data. The drop in DO in treatment 2G indicated that oxygen also diffuses through the teflon

septa. Based on this loss, the decrease in DO in treatments 2G and 2H was not attributed solely to microbial activity. The diffusion of oxygen across the teflon septa may also account for the increased degradation of the solutes in this study. In general, two parts of oxygen are required to remove one part of hydrocarbon. Using these calculations, the microcosms should have been oxygen limited. The absence of oxygen limitation, particularly in treatments with no added source of oxygen, was likely the result of oxygen diffusion into the microcosms. This suggests that in future studies, a more suitable microcosm should be employed.

5.10.6 Discussion of Batch Biodegradation Data

The rates of biodegradation (k values and half-lives) were highest in both biodegradation experiments with air augmentation (1A and 2A) or with the addition of oxygen (2G). Almost complete degradation (to below detection limit or less than 2 ug/L) was shown in each case. These data indicated that the limiting substance was oxygen. Analysis of water quality data supports this hypothesis. Total phosphate in the groundwater averages 0.6 mg/L and nitrate averages 0.25 mg/L.

Addition of NH_4Cl to the microcosms may have spurred the process of nitrification. This would account for the reduction in dissolved oxygen values without the concomitant loss of hydrocarbons. This effect was seen in treatment 2B. In this case, the DO dropped from 7.5 to 2.5 mg/L with no loss in hydrocarbon concentration. The presence of nitrate

in the aquifer at the Lake Alfred site and the low dissolved oxygen levels in the aquifer indicate that there may be significant levels of nitrifying bacteria which may be stimulated by the addition of NH_4Cl. Indirect evidence for this hypothesis is seen in the results of the INT studies for treatments 2A and 2B. Treatment 2B showed a seven-fold increase in electron transport activity although there was no substantial decrease in hydrocarbon concentration (Figure 5-22).

The microorganisms in this study are able to degrade aromatic hydrocarbons rapidly down to the 1 ug/L range given sufficient oxygen. These data confirm the work of Jensen et al. (1985) who show the degradation of aromatic hydrocarbons in petroleum contaminated groundwater to 1 ug/L or less. The rates of biodegradation determined from these batch biodegradation studies were significantly faster than that of Kappeler and Wuhrmann (1978b). In that study benzene required 12 days to degrade completely. Delfino and Miles (1985) showed an eight day lag phase for benzene dosed to clean groundwater. In this study, benzene was completely removed in a minimum of two days, indicating the adaptation of bacteria from the Lake Alfred site to degrade aromatic hydrocarbons.

5.10.7 Hydrogen Peroxide

The introduction of hydrogen peroxide into the microcosms produced a lag phase. The microbial populations required several days to adapt to the changing environmental

ug INT / gram dry weight soil
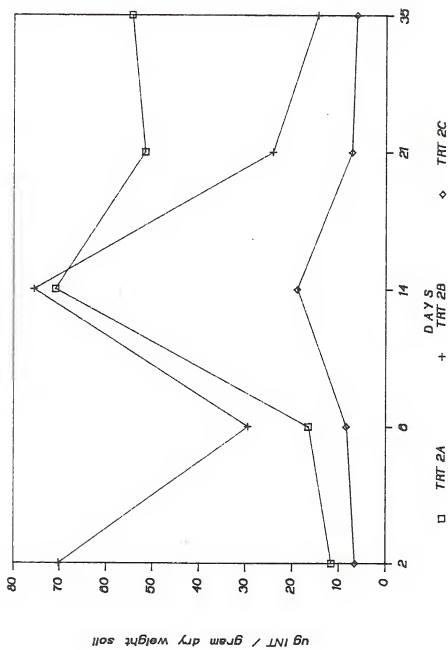
Figure 5-22. Electron transport activity in biodegradation treatments 2A, 2B and 2C.

conditions. This was reflected in the electron transport activity graphs where H_2O_2 treatment reduced INT-formazan production. This may result from the toxicity of H_2O_2 to the microbial population.

The addition of hydrogen peroxide to the batch microcosms did increase the DO, especially in biodegradation experiment #1. Initial DO levels were increased by 2 to 3 mg/L following addition of H_2O_2 in treatments 1B and 1C. However, hydrogen peroxide treatment did not increase the rates of degradation, or improve the extent of removal of aromatic hydrocarbons. Air or oxygen addition was shown to be more effective methods of oxygen supplementation, since they did not require an adaption period.

This conclusion may not be significant under field conditions, where an adaption period may not be an important drawback, given the economy of H_2O_2 relative to air or oxygen addition. These studies demonstrate that H_2O_2 does not limit the extent of biodegradation, but that there is an adaption period associated with its use. No column experiments were performed with hydrogen peroxide. These experiments would have assessed hydrogen peroxide reactivity under flowing conditions.

5.11 Column Biodegradation Experiments

Several authors employed flow-through soil columns to study the degradation of organic contaminants (Kuhn et al., 1985). Kuhn et al. (1985) noted that if one expects to

apply laboratory derived rate constants to field conditions that input concentrations should be similar to field concentrations. The columns used in this work were packed with soil from the Lake Alfred field site, and were supplied with well water from Lake Alfred so that field and laboratory conditions were closely matched. Two flow rates were used to better simulate the varied flow conditions present in the Lake Alfred aquifer.

The results of the columns run at low flow velocities (0.01 cm/min) are shown in Figure 5-23. These data were analyzed to determine rate constants, and these are shown in Table 5-22. The rate constants were calculated with equation [4.7]. The rates of degradation were much higher in the column system than in the batch biodegradation system. The rate constants of the aromatic compounds in the column system were one to two orders of magnitude greater than batch study constants. The increased rate of hydrocarbon removal was the result of improved transport of carbon sources, nutrients and oxygen to the microbial community in the column system. The microcosms in the batch studies were not continuously mixed so that portions of the microcosm may have been nutrient or oxygen limited. Removal efficiencies of 85-95% were seen for all compounds except for benzene, which was degraded more slowly and showed a 60% percent removal. The order of degradation was m,p-xylene > ethylbenzene > o-xylene > toluene > benzene. This order was
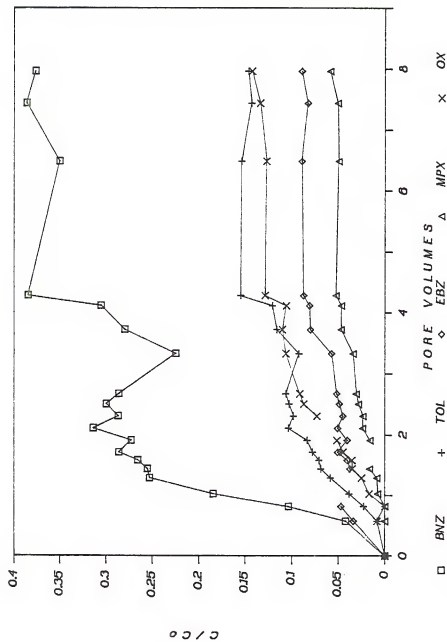
Figure 5-23. Breakthrough curves for aromatic compounds in column biodegradation experiments performed at a flow rate of 0.90 mL/hr.

Table 5-22. First order biological rate constants and
half-lives of aromatic hydrocarbons for the
biodegradation column with flow at 0.90 mL/hr.

Compound	C/Co	k^a day^{-1}	$t_{1/2}$ day
Benzene	0.36	5.80	0.120
Toluene	0.144	11.01	0.063
Ethylbenzene	0.086	13.94	0.050
m,p-Xylene	0.051	16.82	0.041
0-Xylene	0.128	11.69	0.059

[a]calculated from the following data:

    length = 2.5 cm
    bulk density = 1.8 g/mL
    particle density = 2.6 g/mL
    pore water velocity = 14.21 cm/day
    volumetric water content = 0.31

consistent with the removal of side chains prior to attack on the aromatic nucleous.

Degradation rates for columns run at the higher flow rate are shown in Table 5-23. The faster flow rate decreased the half lives of the aromatic contaminants. This resulted from improved transport of oxygen and subtrate. The flow rate used in this column was equivalent to groundwater velocities in portions of the Lake Alfred aquifer (Killan, 1987) and may closely reflect field removals. Breakthrough curves for benzene, toluene and 1,2,4-trimethylbenzene are shown in Figures 5-24 ,5-25 , and 5-26. Only 10% of the benzene and 30% of the toluene were removed at this flow rate although other removals are in the range of 50-60%. The difference in the degradation for benzene is seen by comparison of Figures 5-24 with Figure 5-26. Benzene almost breaks through the column completely, reflecting the time involved for the microbes to degrade this solute. The branched aromatic compounds are more rapidly degraded, which is consistent with the results from the 0.680 cm/min column. The rates of degradation of the aromatic compounds in the 0.01 cm/min columns were in the order $C_9 > C_8 > C_7 > C_6$. Benzene was the most recalcitrant with a half life of 0.12 days (2.88 hours). These data are consistent with the aromatic degradation process described by Evans (1977), and the literature on the fate of aromatic hydrocarbons in soils (Bossert and Bartha, 1984).

Table 5-23. First order biological rate constants and
            half-lives of aromatic hydrocarbons for the
            biodegradation column with flow at 1 mL/min.

Compound	k^a day^{-1}	$t_{1/2}$ day
Benzene	17.7	0.040
Toluene	71.1	0.010
Ethylbenzene	125.3	0.006
m,p-Xylene	133.1	0.005
o-Xylene	115.2	0.006
Isopropylbenzene	166.7	0.004
n-Propylbenzene	192.4	0.004
3 or 4 Ethyltoluene	172.4	0.004
1,3,5-Trimethylbenzene	178.1	0.004
2-Ethyltoluene	158.4	0.004
1,2,4-Trimethylbenzene	172.3	0.004
1,2,3-Trimethylbenzene	150.6	0.005

[a]calculated with the following data:

    length = 5.0 cm
    pore water velocity = 0.680 cm/min
    particle density = 2.6 g/mL
    bulk density = 1.82 g/mL
    volumetric water content = 0.30
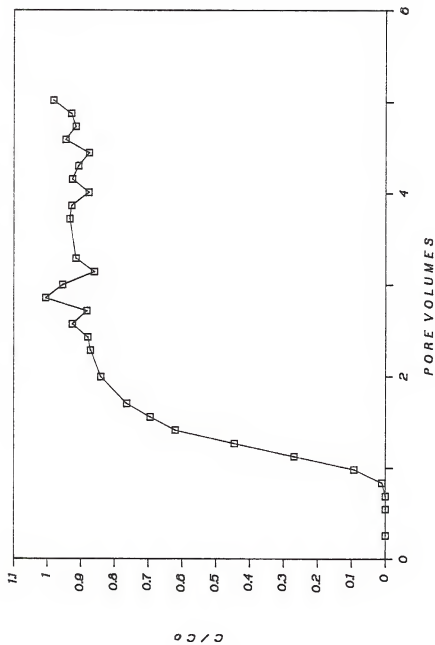
Figure 5-24. Breakthrough curve for benzene in column biodegradation experiment performed at a flow rate of 1 mL/min.
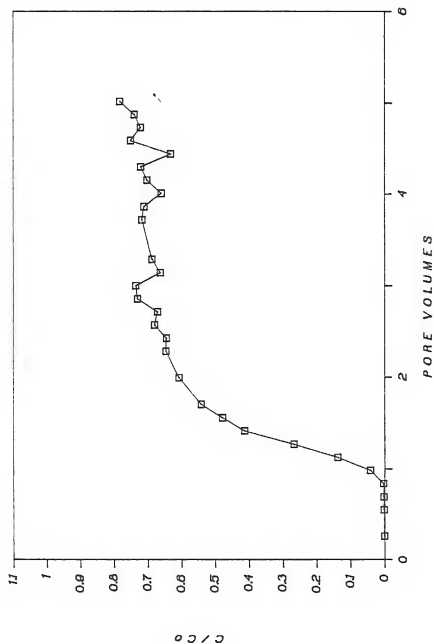
Figure 5-25. Breakthrough curve for toluene in column biodegradation experiment performed at a flow rate of 1 mL/min.
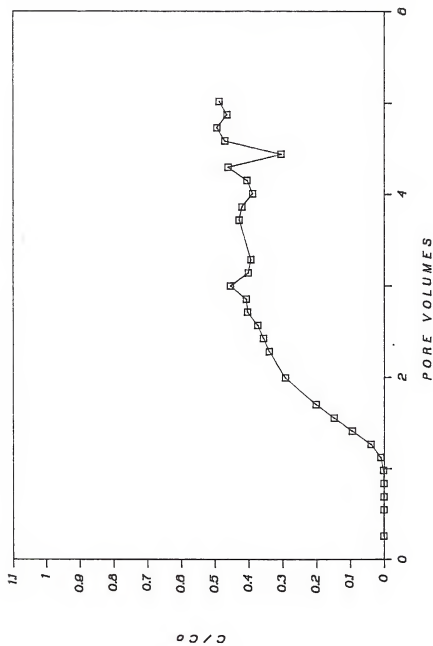
Figure 5-26. Breakthrough curve for 1,2,4-trimethylbenzene in column biodegradation experiment performed at a flow rate of 1 mL/min.

Based on these data, it is evident that a well adapted, standing microbial population from Lake Alfred is capable of degrading aromatic hydrocarbons at relatively high loadings and short contact times. Degradation may be aided by the development of an efficient biofilm (Bouwer and McCarty, 1984). Benzene was degraded to a lesser extent than the alkyl aromatics and o-xylene was more resistant to microbial degradation than the meta and para isomers. Kuhn et al. (1985) in column studies with all three xylene isomers noted the same phenomenon. The increased resistance of o-xylene was also seen in the batch biodegradation data presented in this study.

In the batch studies, benzene was degraded at higher rates than most of the branched aromatic compounds. This is contrary to the column data. This difference in removal rates may be the result of longer contact time in the batch studies. This phenomenon has important consequences for the degradation of hydrocarbons in field studies, where high flow rates may provide insufficient contact time for biological removal. Flow rates were seen to significantly affect the rates of degradation in the experimental column system. The half life for benzene decreased from 0.120 days at 0.01 cm/min to 0.039 days at a flow velocity of .680 cm/min. The half life for toluene decreased from 0.063 hours to 0.0097 hours.

However, these rates are derived from non-limiting conditions and these data may not completely represent

biodegradation in the field, where oxygen limitation reduces the biological removal of hydrocarbons.

The rapid biodegradation of solutes in the batch and column biodegradation studies supports the hypothesis that the microbial community in the Lake Alfred aquifer is well adapted to remove aromatic hydrocarbons from gasoline sources. In instances where adaptation has occurred, biotransformations may be so rapid that they are considered instantaneous relative to the rate of groundwater flow. This shifts the quantitative prediction of biological activity from a consideration of biological kinetics to a consideration of the extent of utilization (Wilson et al., 1983b). Thus geochemical constraints become the controlling factors in the biodegradation process. This is the situation at the Lake Alfred site, where oxygen is the limiting substance.

5.12   Field Data

It is beyond the scope of this work to thoroughly describe all the field data collected during the past 18 months. Rather, the major findings of this dissertation will be correlated with selected aspects of the field data. These topics include analysis of field-scale dispersion, field-scale solute transport and the enumeration of microbial populations.

5.12.1 Dispersion

The breakthrough curve for the NH_4Cl tracer at the Lake Alfred site is shown in Figure 5-27. The dispersion coefficient calculated from these data was 0.546 cm^2/min. Compared with the dispersion coefficients from the column experiments performed at 0.680 cm/min (0.01-0.07 cm^2/min), the field scale dispersion is an order of magnitude larger than the column data. The calculated P_e is approximately 25. This value should be useful in the modeling of the Lake Alfred aquifer.

5.12.2 Solute Transport

An analysis of solute transport at the Lake Alfred research site is hampered by geologic and man-made obstacles. The presence of a swale running through the site and of a dual flow pattern around the pump house (Building 12) have produced preferential flow in the aquifer. Also, sewer, drainage, steam and telecommunications lines criss-cross contaminated portions of the aquifer, complicating the flow path of dissolved hydrocarbons. It is also probable that gasoline storage tanks in between Buildings 10 and 12 and transfer equipment south of the wash rack added unknown quantities of gasoline to portions of the study area (Killan, 1987). This skews the distribution of hydrocarbons in the aquifer and makes determination of solute transport difficult. Finally, the pumping wells (UF-2M, RAP-1 and RAP-3) distort the transport of contaminants. Less retarded solutes appear to be more retained by reversal of
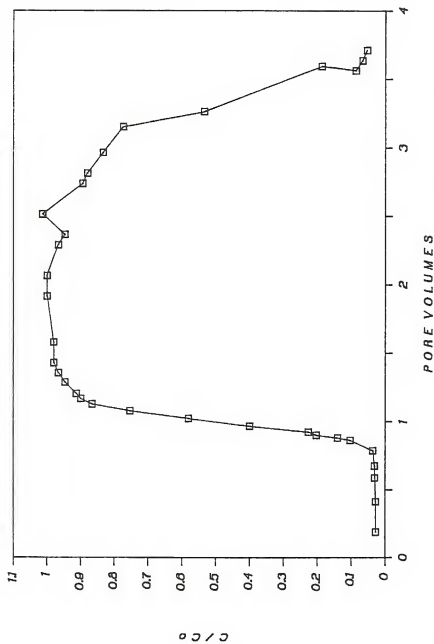
Figure 5-27. Breakthrough curve for field tracer (NH_4Cl) experiment measured at RAP-10.

the hydraulic gradient. Conversely, solutes which are more highly sorbed move more quickly towards the pumping wells as a result of increased convective flow of the mobile phase (ie., groundwater). With these caveats in mind, interpretation of the field data becomes very complex.

The distribution of benzene at the field site is highest toward the swamp (well UF-3W) as is shown in Figure 5-28. The major concentrations of benzene seem to have migrated substantially faster than the other compounds. This is expected from the relatively low retardation factor demonstrated in the laboratory studies, and also from the inefficient biodegradation of benzene at high flow, as determined in the biodegradation column run at 0.680 cm/min. In this column, only 10% of the benzene was removed, whereas the branched aromatics were more easily degraded.

Hydrocarbon data from each monitoring well are presented in Appendix G. Examination of these data demonstrate that the areal distribution of other aromatic solutes are less distinct than benzene. Analyses of these data do not yield a sequential distribution of compounds suggested by retardation factors found in laboratory experiments. This results from the increased susceptibility to microbial attack, and the probability of multiple spill sites.

Ortho-xylene (Figure 5-29) has a measured retardation factor of 1.6, which is 20% larger than that of benzene. However, the areal distribution of o-xylene is much
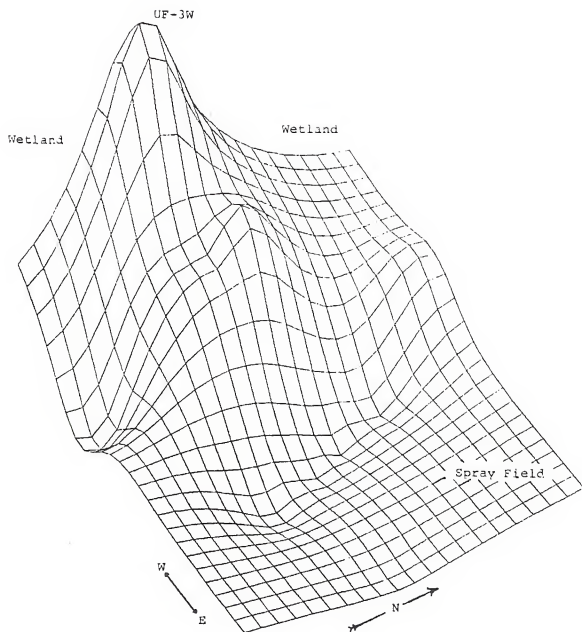
Figure 5-28.   Distribution of benzene (ug/L) at the
Lake Alfred field site.
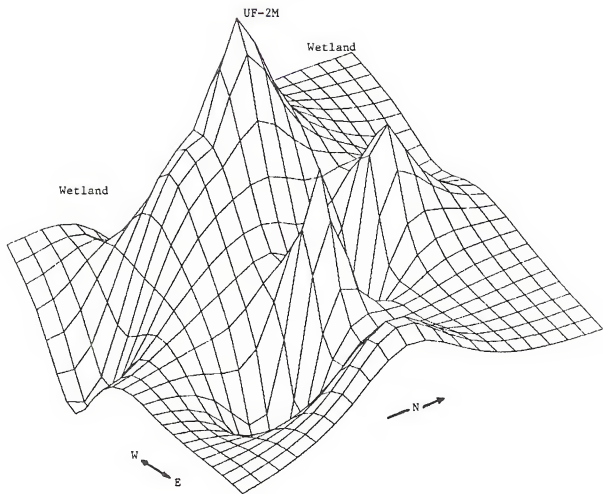
Figure 5-29. Distribution of o-xylene (ug/L) at the
Lake Alfred field site.

different than that of benzene. Based on a comparison of R values, the distribution of o-xylene should be skewed towards the wetlands, as is benzene. One factor which may account for the apparent increase in retardation for o-xylene is the higher rate constant for biological removal (half life = 0.144 hours at 0.680 cm/min) compared to benzene (0.940 hours). This results in improved removal of o-xylene as it moves through the aquifer, so that the solute front appears retarded, relative to benzene. These type of analysis, although somewhat crude, indicates the importance of biological data in the interpretation of solute transport under field conditions.

5.12.3 Microbial Enumeration and biodegradation

Microbial populations at the field site are given in Tables 5-24 to 5-27. Generally they range from 10^5 to 10^6 organisms/gram dry weight soil. Given sufficient oxygen, this population is sufficient for complete biodegradation as shown in the batch laboratory studies; no additional nutrients are necessary. The extent of oxygen limitation is noted in Table 5-28, where the range in concentrations of DO over the study period are presented. Wells which exhibit low DO also exhibit high concentrations of hydrocarbons. An example of the apparent lack of significant bioactivity is seen in an examination of well data from OHM-3. This well shows consistently low DO (0.4 mg/L), with no significant changes in the concentrations of any of the individual solutes.

Table 5-24. Microbial populations in a soil core
            taken south of the paint shop (Bldg. 54),
            June, 1986.

Depth, feet	CFU/gdw[a] x 10^5	
	avg.	std. dev.
4.15	4.00	1.53
4.67	5.28	0.72
5.46	3.07	0.56

[a]CFU/gdw: colony forming units per gram dry weight

Table 5-25. Microbial populations in a soil core
            taken in the spray field, June, 1986.

Depth, feet	CFU/gdw[a] x 10^5	
	avg.	std. dev.
0.5	82.3	5.18
1.0	30.8	0.54
1.5	8.77	0.66
2.0	4.21	0.36
3.0	4.59	2.83

[a]CFU/gdw: colony forming units per gram dry weight

Table 5-26. Microbial populations in a soil core
taken south of the pump house (Bldg. 12),
July, 1986.

| Depth, feet | CFU/gdw x 10^6 | | Comments |
	avg.	std. dev.	
0.5	3.6	0.73	
1.0	4.6	1.21	
1.5	6.0	2.25	
2.0	2.6	0.36	
2.5	2.1	0.91	
4.0	4.5	2.16	
5.0	1.6	0.16	
6.0	3.3	0.60	Saturated zone gasoline odor

Table 5-27. Microbial populations from samples
collected during installation of
monitoring wells RAP-5 and RAP-6,
September, 1986.

	CFU/gdw x 10^6				
Depth, feet	RAP-4		RAP-5		
	avg.	std. dev.	avg.	std. dev.	Comments
2.0	ns[a]	ns	4.9	0.34	
3.0	8.9	0.96	3.2	0.25	
4.0	4.1	0.22	3.1	0.82	
5.0	ns	ns	8.4	0.31	
6.0	4.2	0.11	2.0	0.85	Saturated zone

[a]no sample

Table 5-28. Water chemistry parameters from selected monitoring wells at Lake Alfred CREC, 1986.

Well	Chloride, mg/L	Conductivity, umhos	pH	Dissolved Oxygen, mg/L	Total Phosphate, mg/L	Nitrate, mg/L
OHM-1	–	270– 302	6.1–6.6	0.2–0.7	0.19	–
OHM-2	793	2100–2700	6.1–6.9	0.2–0.7	1.40	0.94
OHM-3	18	350– 390	5.9–6.6	0.1–0.3	0.62	0.14
OHM-4	16	290– 333	6.1–6.7	0.2–0.3	0.40	0.20
P-5	19	340– 390	6.1–6.7	0.2–0.6	0.47	0.19
P-6	19	245– 300	6.4–7.2	0.4–0.8	0.33	0.22
P-7	21	278– 410	5.8–7.1	0.3–0.4	0.34	0.24
UF-1E	21	270– 353	5.8–6.6	0.9–3.5	0.47	–
UF-2M	12	315– 382	5.4–6.7	0.7–0.8	0.58	0.14
UF-3W	16	470– 700	6.1–6.7	0.1–0.5	0.82	0.19
RAP-2	22	278– 325	6.1–7.1	0.9–4.1	0.65	0.29
RAP-4	–	300– 319	6.1–6.9	0.5–1.8	0.53	–
RAP-5	–	262– 280	5.8–6.9	0.2–2.2	0.57	0.15
RAP-6	–	290– 317	6.2–7.1	1.4–3.9	0.65	0.41
RAP-7	0	315– 325	6.3–7.1	1.7–4.8	0.67	0.43

The opposite appears to be true in data from well P-7. This well shows significant decreases in some aromatic hydrocarbons, and the dissolved oxygen levels start to increase after November, 1986. This may be the result of the increased recharge of aerated water and change in pumping conditions established by Killan (1987). Decreases in hydrocarbon concentrations concomitant with increasing DO are also noted up gradient of P-7 prior to November 22, 1986. Wells RAP-6 and RAP-5 exhibit rapid removals of hydrocarbons following the start of increased flushing with aerated water (22 October, 1986). However, the data are insufficient to conclude whether this change results from the increased supply of oxygenated water and subsequent biodegradation, or if it is caused by the more rapid solute transport owing to increasing the flow velocity of the aquifer.

CHAPTER VI
SUMMARY AND CONCLUSIONS

6.1 Summary

Hydrolysis, sorption and biodegradation reactions of
aromatic hydrocarbons (all isomers of $C_6H_6-C_9H_{12}$) under
water saturated soil conditions were investigated. Several
treatment techniques (H_2O_2, O_2 gas and NH_4Cl) were evaluated
to enhance the microbial degradation of the aromatic
compounds. These studies were performed with a
multicomponent solute system of aromatic hydrocarbons,
resulting from the partial solubilization of gasoline into
groundwater, obtained from a field site where a gasoline
spill had occurred. The sorbent used in these studies was
collected from the field site in a non-contaminated portion
of the aquifer. This site was typical of sandy surficial
aquifers in Florida, and was characterized by the low
organic carbon content (0.015%) of the aquifer material.
The aquifer was composed primarily of medium to fine grained
sands.

Contaminated well water from the surficial aquifer was
employed as the source of solutes for the majority of
experiments. The major components of this water were the
hydrocarbons ($C_6H_6-C_9H_{12}$) used in this study.

168

6.1.1 Hydrolysis studies

Hydrolysis did not account for substantial losses of the aromatic hydrocarbons in this study. These solutes were resistant to hydrolysis even under extreme (relative to the environment) conditions of pH (2,9,12) or temperature (60 C).

6.1.2 Sorption studies

Sorption of C_6-C_9 aromatic solutes to the aquifer material employed in this work was relatively rapid. Rate studies to determine the approach to equilibrium revealed that there was an initial period of rapid sorption and that equilibrium conditions were established within four to eight hours.

Multicomponent sorption experiments of the dissolved aromatic hydrocarbons in this study were performed in batch isotherms and in leaching column experiments. Surficial well water was used as the source of these solutes. Aquifer material from the Lake Alfred site was used as the sorbent. Batch sorption employed a 3:1 solids to solution ratio to approximate aquifer conditions, and to maximize the change in solution concentration resulting from sorption of the solutes to the aquifer material. Equilibrium batch isotherm data was evaluated with the Freundlich model, the linear model and the linear model with suppressed intercept. Sorption coefficients (K_d) for the two linear models were equivalent, and the Freundlich model gave similar sorption coefficients (K_f). K_d values from the linear models ranged

from 0.49 for toluene to 0.142 for 1,3,5-trimethylbenzene. It was concluded that the sorption process was reversible in these studies with no significant hysteresis.

Column sorption experiments were performed under saturated steady flow conditions. Sorption coefficients from batch isotherm studies and column sorption studies were closely matched. The average dispersion in these columns was 0.044 cm^2/min with a standard deviation of 0.029 cm^2/minute. Retardation factors were determined for all C_6-C_9 aromatic compounds from the multicomponent system of dissolved aromatic hydrocarbons in well water. Retardation factors ranged from 1.36 for benzene to 2.40 for n-propylbenzene. These data demonstrated the relatively low retardation of aromatic solutes by the aquifer materials. The flow velocity used in the column experiments (0.680 cm/min) was close to seepage velocities measured at the field site (0.02-0.38 cm/min). The column breakthrough curves (BTC) exhibited some non-equilibria as a result of slow sorption kinetics, and this process may also affect the transport of solutes in the field.

The influence of competing solutes was investigated by comparing retardation values for benzene in a single solute system with the breakthrough curve for benzene in the multicomponent system. The retardation factors for benzene in both column systems were similar (1.36 vs. 1.40). Solute competition for sorbing sites was not a significant factor

in this study. This was likely the result of the use of low concentrations (less than 2% of the water solubility).

Sorption mechanisms were evaluated by comparison of K_{oc} data from column studies in this study with partitioning and molecular topology models. Regression analysis of K_{oc} data versus literature values for K_{ow} demonstrated that partitioning alone did not adequately describe the sorption process ($r^2 = 0.857$). Regression analysis of K_{oc} data with first order molecular connectivity indices indicated that sorption may be partially described as a surface area dependent phenomena ($r^2 = 0.839$). Both models gave equivalent fit to the K_{oc} data, and this suggested that sorption was the result of several processes.

6.1.3 Biodegradation Studies

Rate constants for the biodegradation of selected aromatic hydrocarbons were determined from batch and column studies. Column studies yielded higher rate constants than the batch studies indicating more rapid removal of solutes. Half lives for columns run at 0.01 cm/min were between 0.120 days for benzene to 0.041 days for m,p-xylene. Rate constants derived from columns with velocities of 0.680 cm/min were higher, indicating increased removal of hydrocarbons. These half lives ranged from 0.940 hours for benzene to 0.086 hours for n-propylbenzene. The increased removal at the higher flow rate was the result of improved transport of oxygen and nutrients to the microbes. The 1 mL/min flow rate (0.680 cm/min) was equivalent to seepage

velocities at the field site, and suggested that the contact time was suitable for complete degradation of aromatic solutes, under non-limiting conditions. This indicated the need for oxygen augmentation at the field site to increase the biodegradation rates of aromatic contaminants.

Batch biodegradation experiments were performed to assess the efficacy of various methods to increase the biological degradation of dissolved aromatic hydrocarbons at the Lake Alfred field site. Laboratory experiments with hydrogen peroxide indicated the ability of the microbial community and the aquifer materials to catalyze the reduction of hydrogen peroxide to yield oxygen gas. No hydrocarbon oxidation was apparent as a result of the hydrogen peroxide decomposition.

The half lives for biological removal of the selected aromatic hydrocarbons with the addition of air (7-8 mg/L O_2) in the batch biodegradation studies (Treatment 1A, Thomas slope rate equation) ranged from 2.91 days for toluene to 4.96 days for 1,3,5-trimethylbenzene. Benzene, toluene and 1,2,4-trimethylbenzene were degraded most rapidly. Augmentation of oxygen in the form of air or oxygen gas was most effective for increasing the biodegradation of aromatic hydrocarbons. These data indicated that the microbes from the Lake Alfred site were well adapted to aromatic gasoline hydrocarbons, and were limited only by the availability of oxygen. Treatment with hydrogen peroxide (17 mg/L to 68 mg/L) increased the dissolved oxygen levels in the

microcosms, but did not increase the rates of degradation or the extent of hydrocarbon removal in batch studies. Ammonium chloride addition produced conditions favorable to nitrifying bacteria, which resulted in the depletion of oxygen without substantial hydrocarbon removal. Treatment with ammonium chloride resulted in a lag phase, during which the microbial community adapted to the changed nutrient conditions. The combination of NH_4Cl and H_2O_2 exhibited a toxic effect to the microflora from the Lake Alfred aquifer. This suggests that the use of NH_4Cl as a field tracer should not be followed by application of H_2O_2 to increase dissolved oxygen. Treatment with H_2O_2 at concentrations of 17 mg/L and 68 mg/L produced lag times of up to eight days, with slightly reduced rate constants.

VOA vials were employed as microcosms for the batch biodegradation experiments. These vials allowed substantial abiotic losses of solutes, as determined by control samples, and were not recommended for use in future experiments.

6.1.4 Microbial Field Data

Oxygen was the limiting substance at the Lake Alfred Site. Dissolved oxygen concentrations in the main area of hydrocarbon contamination was only 0.1 to 0.4 mg/L. The average value for total phosphorus was 0.6 mg/L and the average value for nitrate was 0.3 mg/L over the study area. These data indicate that there were sufficient phosphorus and nitrogen sources to initiate the biological removal of hydrocarbons, given sufficient oxygen. This hypothesis was

confirmed by the laboratory biodegradation experiments, where the microbes from the field site were well adapted and were able to rapidly degrade the aromatic solutes to less than 0.5 ug/L. Microbial populations at the field site were determined to be in the range of 10^5 to 10^6 organisms per gram dry weight of soil.

6.1.5 Field Scale Solute Transport

The distribution of contaminants at the Lake Alfred field site was complicated by physical structures, numerous spills and underground utilities. This made the interpretation of field data difficult. The major concentrations of benzene were found at the western boundary of the field site, down gradient from the spill area. This distribution of benzene demonstrates that the combination of low retardation and inefficient biodegradation can result in increased migration, relative to solutes which were more retarded and more easily degraded.

6.2 Conclusions

1. Hydrolysis was not a significant removal mechanism for aromatic hydrocarbons.

2. Solute-sorbent equilibrium was established in batch sorption vials in four to eight hours.

3. Equilibrium batch sorption isotherms were linear.

4. Column breakthrough curves exhibited apparent nonequilibria.

5. Solute-solute competition for sorbing sites was not observed.

6. Equilibrium batch sorption isotherm data and breakthrough curve data yielded similar estimates of solute retardation and sorption.

7. Partitioning models and the first order molecular connectivity model gave equivalent fit to the sorption data. This supports the hypothesis that sorption results from several processes depending on the sorbent and the solute.

8. Bacteria from the Lake Alfred site are adapted to aromatic hydrocarbons from gasoline sources.

9. Enzymatic and nonbiological hydrogen peroxide catalysts are present at the Lake Alfred site.

10. Hydrogen peroxide does not oxidize aromatic hydrocarbons.

11. Addition of air or oxygen gas was the most effective method for stimulating microbial degradation of the solutes in this study.

12. Hydrogen peroxide was effective in increasing the dissolved oxygen level in the microcosms.

13. Hydrogen peroxide addition to the microcosms did not increase the rate or extent of aromatic hydrocarbon removal.

14. Ammonium chloride addition to the microcosms caused nitrification, resulting in oxygen consumption in the microcosms without hydrocarbon removal.

15. The combination of ammonium chloride (18 mg/L) and hydrogen peroxide (17 mg/L) additions to biodegradation microcosms produced toxic conditions.

16. Column biodegradation studies yielded higher rate constants than the batch studies, reflecting improved transport of nutrients and oxygen to bacteria.

17. Rates of biodegradation for aromatic compounds were in the order $C_9 > C_8 > C_7 > C_6$. Benzene was the most recalcitrant solute in the column studies.

18. Benzene, toluene, m,p-xylene and 1,2,4-trimethylbenzene showed the most rapid biodegradation in the batch studies.

19. Microbial communities in the Lake Alfred aquifer were in the range of 10^5-10^6 colony forming units per gram dry weight of aquifer material.

20. Microbial populations at the Lake Alfred site were oxygen limited, but not phosphorus or nitrogen limited.

21. Horizontal dispersion at the field site was calculated to be 0.546 cm^2/min.

22. Low retardation (1.36), high flow velocity (0.680 cm/min) and a degradation rate of 17.65 ug/L/day explain the distribution of benzene at the field site.

APPENDICES

APPENDIX A
CHROMATOGRAPHIC CONDITIONS AND QUALITY CONTROL
PARAMETERS FOR THE ANALYSIS OF AROMATIC HYDROCARBONS

This appendix lists the chromatographic conditions used in the gas chromatographic analysis of aromatic hydrocarbons on the Perkin Elmer 4100 gas chromatograph. Following the GC parameters, summary quality control data is presented for chromatographic analyses performed during the course of these studies.

```
METHOD 6   ANGLEY 2      DATE LAST WRITTEN 87/05/12

SECTION 1  GC CONTROL

                              1       2       3       4
    OVEN TEMP (DEG C)        50      70      94     200
    ISO TIME (MIN)          5.0     7.0     0.0     0.0
    RAMP RATE (DEG C/MIN)   3.0     3.0    30.0

    FID SENS   HIGH

    DET ZERO   ON

    DET TEMP   300

    FLOW  A  55 ML/MIN
    CARRIER GAS HE

    EQUILIB TIME    0.5 MIN
    TOTAL RUN TIME  30.1 MIN

SECTION 2  TIMED EVENTS

    TIME    EVENT

    0.01    WIDTH      5
    0.02    SET ZERO
   29.00    INTEG    OFF

SECTION 3  DATA HANDLING

    DATA ACQUISITION                  REPORT

    START TIME   0.00 MIN           CALC TYPE     INT STD
    END TIME    30.19 MIN           AREA/HT CALC  AREA
                                    PRINT TOL     0.0000
    WIDTH           5               OUTPUT
    SKIM SENS     100                 SCREEN      NO
    BASELINE CORP  B-B                PRINTER     YES

    AREA SENS     119
    BASE SENS       6

    PEAK IDENTIFICATION              QUANTITATION (CALIB AUG OF 12)

    UNRETD PEAK TIME   0.00 MIN      SCALING FACTOR     1.0000
    AREA/HT REJECT     0.0000        RF FOR UNKNOWNS   10.0000

    REF PK: TIME      13.19 MIN      STD COMPNT NAME    CHLOROBNZ
            TIME TOL   0.05 MIN      SMP AMOUNT         1.0000
                                    STD AMOUNT        52.0000
    COMPNT: TOL ABS    0.05
            TOL %      0.50

    COMPONENT LIST

    RT       RF      STD AMT   NAME             GRP

    5.63    7.4916    7.1424   BENZENE           1
    9.68    7.5224    4.8768   TOLUENE           1
   13.56   10.0000   52.0000   CHLOROBNZ         0
   14.82    7.6000    5.4360   ETHYL BENZENE     1
   15.48    7.6960    5.5080   M,P XYLENE        1
   17.25    7.9968    5.6328   O XYLENE          1
   20.25    7.3722    5.6040   ISOPROPYL BNZ     2
   22.60    7.5404    4.1806   N PROPYL BNZ      2
   23.38    6.7646   11.0616   3,4 ETHYLTOL      2
   24.00    6.7483    3.2520   1,3,5 T M BNZ     2
   24.70    6.7756    5.1312   O,ETHYLTOLUENE    2
   25.80    7.4867    4.1664   1,2,4 TMBNZ       2
   27.44    7.9088    5.2440   1,2,3 TMBNZ       2
```

Precision and accuracy data for the analysis of aromatic hydrocarbons in groundwater by EPA method 602, (modified).

Compound	Precision % RSD,	sd	Accuracy % R,	sd
Benzene	6.6,	8.7	98.0,	13.4
Toluene	6.2,	9.3	99.3,	18.0
Ethylbenzene	5.1,	7.0	95.2,	12.7
m,p-Xylene	4.2,	4.2	95.3,	12.1
o-Xylene	4.8,	4.7	100.8,	15.9
Isopropylbenzene	5.8,	13.2	89.8,	11.3
n-Propylbenzene	5.7,	8.3	86.5,	10.7
3,4-Ethyltoluene	4.5,	6.1	90.4,	10.2
1,3,5-Trimethylbenzene	7.3,	16.2	89.6,	12.7
2-Ethyltoluene	4.0,	4.7	83.8,	10.2
1,2,4-Trimethylbenzene	4.4,	3.6	90.0,	15.2
1,2,3-Trimethylbenzene	6.1,	5.5	93.0,	12.2

APPENDIX B
FIELD SAMPLING PROCEDURES

The sampling procedures employed during this research
were described in the Lake Alfred Quality Assurance/Quality
Control (QA/QC) plan (Killan, 1987). Section six of the QA/QC
plan is presented in the following pages.

6.0 SAMPLING PROCEDURES

   6.1 Cleaning Procedures

      6.1.1 Volatile Organics.

         Bottle type: - water: 60 mL glass vial with
                       teflon lined septum caps.
                  - soil: 1 quart mason jars.

         Soap: Alconox

         1) Wash caps, liners and vials in hot soapy
            water.
         2) Rinse liberally with tap and DI water.
         3) Rinse with pesticide grade methanol.
         4) Dry caps, septa, and vials in oven at 105
            C for no more than 60 minutes.
         5) Cool in inverted position, and cap
            immediately when bottles are cool enough
            to handle.

      6.1.2 Labels

         1) After cleaning the appropriate label is
        attached to each bottle, and the date cleaned
        is entered.

   6.2 Field Documents and Records.

      6.2.1 Field sheets.
         The field sheet (see attachments) is filled
         in with the following information upon
         sampling:
            1) date
            2) time
            3) sample type
            4) preservation
            5) well number (for well samples)
            6) well casing and diameter
            7) depth of water at time of sampling
            8) depth of core (if applicable; soil
               samples)
            9) note special characteristics of
               sample.
           10) field number

         All field measurements are recorded in the
         bound field notebook or on the data sheets.

All samples are assigned a consecutive field number and this is recorded in the field notebook, the field data sheet and on the sample bottle.

6.3 Water Sample collection - Field procedures.

6.3.1 Well preparation.

The volume of water in each well is determined. The well is bailed for three times the calculated volume. This is done using a PVC bailer, or a battery operated pump. The bailed volume is measured in a calibrated container. Glass tubing is attached to the end of tygon tubing to present a glass surface to the water in the well. Tygon tubing is attached directly to the pump. Each well is supplied with a dedicated piece of tygon tubing and a dedicated glass insert.

6.3.2 Volatile Organic Samples

An unopened field blank is taken into the field.

Wells are bailed as above.

Vials are filled by lowering the container directly into the well. The vial is filled to overflowing. The teflon side of the septum is placed on the meniscus, and capped tightly. The sample is inverted and examined for air bubbles.
If air is present the sample is discarded, and the well resampled.
Samples are taken in duplicate and chilled immediately and placed in the dark. Blanks are stored with the samples.

No preservation of the samples other than cooling is performed.

6.4 Soil Sample Collection

6.4.1 Chemical Analysis

Soil samples destined for chemical analysis for gasoline will be collected with a stainless steel auger. Samples will be placed into a one quart mason jar. Samples

will be tightly packed to reduce headspace in the sample container. Samples are transported on ice and stored at 4 C in the dark.

6.4.2 Biological Analysis
Soil samples for biological analysis will be collected with sterilized (100 ppm chlorine solution) stainless steel auger. Samples will be placed in a one quart mason jar, cleaned in the same manner as the described in section 6.1.1. Samples will be stored at 4 C in the dark.

6.5 Measurement of field parameters.

6.5.1 Temperature.
Temperature will be measured in the wells using a thermometer, calibrated against an NBS standard thermometer.

6.5.2 pH.
The pH of the well water will be measured using a portable pH meter (Orion Research model 401) connected to a Fisher AccupHast microprobe combination electrode.

6.5.3 Dissolved Oxygen.
DO will be measured using a portable dissolved oxygen meter (YSI 54A) with a YSI 5739 oxygen probe.

ISOTHERM DATA FOR THE SORPTION OF STUDY COMPOUNDS
TO LAKE ALFRED AQUIFER MATERIAL

Batch isotherm data is presented for each compound in this study. Freundlich isotherms for each compound are also shown.

Benzene Sorption Data

Cs (ug/L) avg	std	Cw (ug/L) avg	std	amount sorbed (ug/L)	amount sorbed (ng/g)	log amount sorbed	log solution concentration
===	===	===	===	===	===	===	===
0.4	0.1	1.5	0.5	1.1	0.38	-0.42	0.18
2.11	0.14	2.7	0.42	0.54	0.19	-0.73	0.42
1.1	0.08	1.5	0.69	0.35	0.12	-0.91	0.16
1.8	0.14	2.5	0.45	0.7	0.24	-0.17	0.4
4.4	a	7.4	0.39	3	1	0.013	0.87
8.7	0.3	15	15.5	66.1	2.1	0.32	1.17
30.9	0.92	73	3.4	41.9	14.5	1.16	1.86
46.19	4.6	90	9	43.8	15.1	1.18	1.95
66	1.6	92	4.4	24.5	9.1	0.96	1.97
254	4.2	338	a	84	29	1.46	2.53
594	12	728	34.3	133	46	1.66	2.86
771	26	865	111	94	32.3	1.51	2.94
873	135	900	90	27	9.5	0.98	2.95

a
n=1

Benzene Desorption Data

Cs (ug/L) avg	std	Cw (ug/L) avg	std	amount sorbed (ug/L)	amount sorbed (ng/g)	log amount sorbed	log solution concentration
===	===	===	===	===	===	===	===
3	1	0.2	0.08	2.8	0.97	-0.015	0.48
92.5	4.4	1.7	1.1	90.3	31.1	1.49	1.96
8.6	1	5.1	0.5	3.6	1.2	0.09	0.93
338	a	106	27	282	97.3	1.99	2.59
865	128	238	a	627	216	2.34	2.94

a
n=1

Freundlich sorption-desorption isotherm for benzene at equilibrium.

Toluene Sorption Data

Cs (ug/L) avg	std	Cw (ug/L) avg	std	amount sorbed (ug/L)	amount sorbed (ng/g)	log amount sorbed	log solution concentration
6.1	0.24	9.9	1.5	3.8	1.3	0.13	0.99
28.9	2.3	49.3	a	20.5	7.1	0.85	1.69
67	17.2	99	a	31.5	10.9	1.04	1.99
166.3	18.9	261	a	95.1	32.8	1.52	2.42
2886	504	4000	a	1114	384	2.58	3.6
3813	79	4069	140	257	88.5	1.95	3.61
209	16	407	14	198	68.3	1.83	2.61
52	a	81	3	29.5	10.2	1	1.91
26	a	41	1.2	14.7	5.1	0.71	1.6
10	1.2	16	0.56	6.4	2.2	0.34	1.21
1.3	0.26	8	0.18	1.7	0.6	-0.22	0.9
4049	155	4566	565	517	178	2.25	3.66
3118	6.8	457	a	138	48	1.68	2.66
4.7	1.2	47	a	4	1.4	0.14	1.66

a n=1

Toluene Desorption Data

Cs (ug/L) avg	std	Cw (ug/L) avg	std	amount sorbed (ug/L)	amount sorbed (ng/g)	log amount sorbed	log solution concentration
295	219	4566	653	4271	1474	3.17	3.66
93	36	1086	a	992	342	2.53	3.04
6	2.8	456	a	450	155	2.19	2.66
1	0.35	46	a	45	15.4	1.19	1.66
784	214	4069	172	3285	1133	3.05	3.61
3	2	406	a	403	139	2.14	2.61
7	a	41	a	34	11.7	1.07	1.61

a
n=1
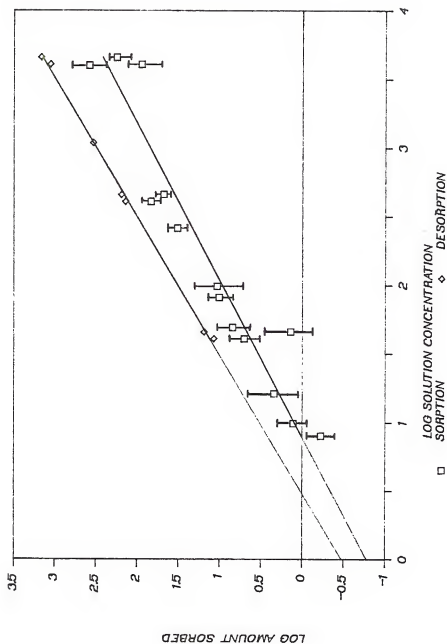
Freundlich sorption-desorption isotherm for toluene at equilibrium.

m,p-Xylene Sorption Data

Cs (ug/L) avg	std	Cw (ug/L) avg	std	amount sorbed (ug/L)	amount sorbed (ng/g)	log amount sorbed	log solution concentration
===	===	===	===	===	===	===	===
3.4	0.2	5.1	a	1.8	0.61	0.21	0.71
13.5	1.2	25.7	a	12.2	4.2	0.62	1.41
35.8	6.3	51.3	a	15.6	5.4	0.73	1.68
80.7	9.2	103	a	21.9	7.6	0.88	1.71
943	456	1026	a	82.9	28.6	1.5	2.63
4.2	0.2	8.6	a	4.4	1.5	0.18	0.93
6.7	0.7	17.1	a	10.5	3.6	0.56	1.23
17.2	0.5	42.9	a	25.7	8.9	0.95	1.92
37.5	0.3	83.7	a	42.3	16	1.2	2.14
176	12	429	1.3	253	87.3	1.94	3.01
3028	102	4290	18.4	1259	434	2.64	3.63
3214	107	4232	184	1081	351	2.54	3.63
1110	37.9	1893	609	783	270	2.43	3.28
300	9.2	423	80	123	42.5	1.63	2.63
110	19.5	137	a	27.5	9.5	0.98	2.01
34.7	2.1	48	1	13.3	4.6	0.66	1.63

a
n=1

m,p-Xylene Desorption Data

Cs (ug/L) avg	std	Cw (ug/L) avg	std	amount sorbed (ug/L)	amount sorbed (ng/g)	log amount sorbed	log amount solution concentration
2055	45.02	4232	609	2177	751.1	2.88	3.63
837	52.88	1893	80	1056	364.3	2.56	3.28
152	20.20	423	a	271	93.5	1.97	2.63
27	0.81	137	a	110	37.9	1.58	2.14
26	3.5	48	1	22	7.6	0.88	1.68
1800	220.02	4287	a	2487	858.0	2.93	3.63
55	50.59	429	18.4	374	129.0	2.11	2.63
19	4.14	86	a	67	23.1	1.36	1.93
13	0.439	43	a	30	10.4	1.01	1.63

a
n=1
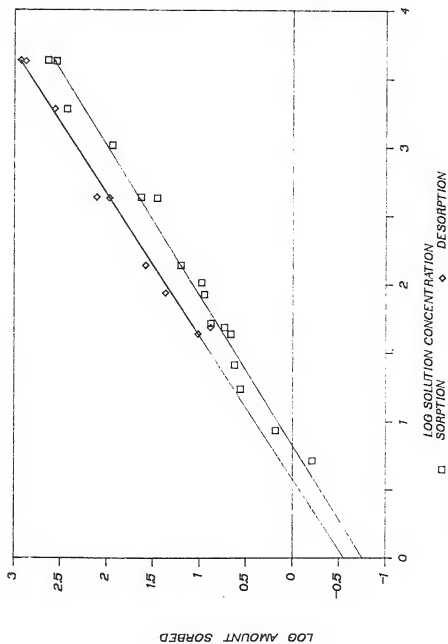
Freundlich sorption-desorption isotherm for m,p-Xylene at equilibrium

LOG SOLUTION CONCENTRATION

□ SORPTION   ◇ DESORPTION

LOG AMOUNT SORBED

o-Xylene Sorption Data

Cs (ug/L) avg	std	Cw (ug/L) avg	std	amount sorbed (ug/L)	amount sorbed (ng/g)	log amount sorbed	log solution concentration
1.49	0.11	2.61	0.53	1.12	0.4	-0.41	0.42
6.32	0.22	11.03	0.24	4.706666	1.6	0.21	1.04
19.70	3.63	23.07	2.15	3.366666	1.2	0.07	1.36
45.53	5.88	105.45	1.56	59.91666	20.7	1.32	2.02
819.42	158.39	1153.58	a	334.5633	115.4	2.06	3.06
2.02	0.13	3.41	a	1.39	0.5	-0.32	0.53
3.10	0.20	6.83	a	3.73	1.3	0.11	0.83
7.95	0.45	17.10	a	9.15	3.2	0.50	1.23
16.80	0.00	34.20	a	17.4	6.0	0.78	1.53
81.23	3.64	170.80	a	89.56666	30.9	1.49	2.23
1274.80	17.77	1708.27	74.22	433.4666	149.5	2.17	3.23
1786.50	74.72	2316.25	257.84	529.75	182.8	2.26	3.36
657.67	20.76	1245.67	137.16	588	202.9	2.31	3.10
176.33	4.64	231.60	0.00	55.26666	19.1	1.28	2.36
56.50	11.50	62.33	3.30	5.833333	2.0	0.30	1.79
19.00	0.82	27.00	0.82	8	2.8	0.44	1.43

a
n=1

o-Xylene Desorption Data

Cs (ug/L) avg	Cw (ug/L) std	avg	std	amount sorbed (ug/L)	amount sorbed (ng/g)	log amount sorbed	log solution concentration
814	126.57	1708	74.22	894	308.4	2.49	2.91
35	11.13	171	a	136	46.9	1.67	1.54
5	0.85	34	a	29	10.0	1.00	0.70
6	5.69	17	a	11	3.8	0.58	0.78
1412	317.35	2316	257.84	904	311.9	2.49	3.15
528	29.95	1246	a	718	247.7	2.39	2.72
91	14.57	168	a	77	26.6	1.42	1.96
16	0.69	61	3.1	45	15.5	1.19	1.20
14	2.01	27	0.82	13	4.5	0.65	1.15

a
n=1
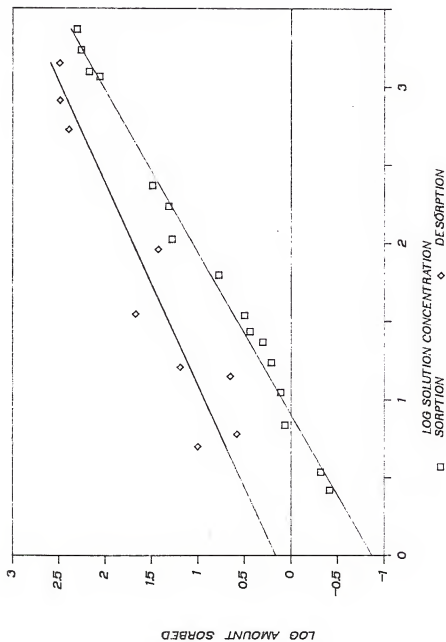
Freundlich sorption-desorption isotherm for o-Xylene at equilibrium.

3,4-Ethyltoluene Sorption Data

Cs (ug/L) avg	std	Cw (ug/L) avg	std	amount sorbed (ug/L)	amount sorbed (ng/g)	log amount sorbed	log solution concentration
758.3	12.34	934.8	517.4	176.5	60.9	1.78	2.97
43.9	3.52	93.5	a	49.6	17.1	1.23	1.97
9	0	18.7	a	9.7	3.3	0.52	1.27
4.1	0.63	9.35	a	5.25	1.8	0.26	0.97
1.97	0.14	3.74	a	1.77	0.6	-0.21	0.57
0.72	0.02	1.87	a	1.15	0.4	-0.40	0.27
532	64	812	133	280	96.6	1.98	2.91
167	7	301	17	134	46.2	1.66	2.48
47	4	81	2	34	11.7	1.07	1.91
14.5	2	18	4	3.5	1.2	0.08	1.26
5	1	9	0	4	1.4	0.14	0.95

a
n=1

3,4-Ethyltoluene Desorption Data

Cs (ug/L) avg	std	Cw (ug/L) avg	std	amount sorbed (ug/L)	amount sorbed (ng/g)	log amount sorbed	log solution concentration
305	7.87	812	133	507	174.9	2.24	2.91
122	10.61	301	17	179	61.8	1.79	2.48
26	2.77	81	2	55	19.0	1.28	1.91
5.44	0.12	18	4	12.56	4.3	0.64	1.26
4.59	0.93	9	0	4.41	1.5	0.18	0.95
145	27.49	935	517.4	790	272.6	2.44	2.97
21	11.67	93.5	a	72.5	25.0	1.40	1.97
5.6	1.39	18.7	a	13.1	4.5	0.66	1.27
3	0.07	9.35	a	6.35	2.2	0.34	0.97

a
a n=1
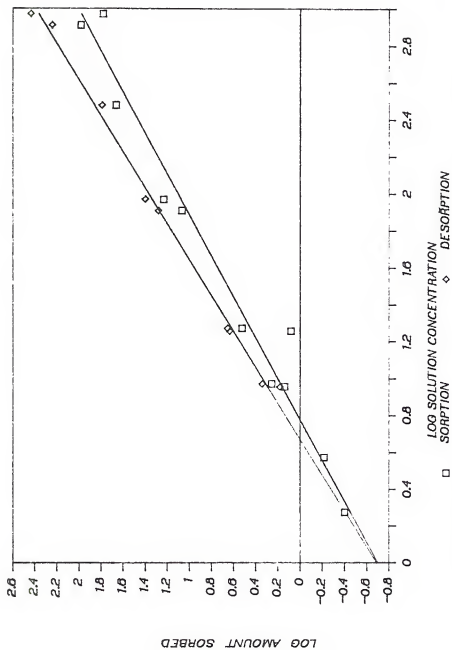
Freundlich sorption-desorption isotherm for 3,4-Ethyltoluene at equilibrium.

LOG SOLUTION CONCENTRATION

SORPTION □ DESORPTION ◇

LOG AMOUNT SORBED

1,3,5-Trimethylbenzene Sorption Data

Cs (ug/L) avg	std	Cw (ug/L) avg	std	amount sorbed (ug/L)	amount sorbed (ng/g)	log amount sorbed	log solution concentration
202	22	326	46	124	42.8	1.63	2.51
70	3	175	30	105	36.2	1.56	2.24
19	1	44	1	25	8.6	0.94	1.64
10	6.4	17.5	3	7.5	2.6	0.41	1.24
2	1	4	a	2	0.7	-0.16	0.60
267.4	4.09	459.7	28.31	192.3	66.3	1.82	2.66
15.8	0.97	45.97	a	30.17	10.4	1.02	1.66
3	0	9	2.11	6	2.1	0.32	0.95
1.3	0.14	4.5	a	3.2	1.1	0.04	0.65
0.65	0.12	2.29	a	1.64	0.6	-0.25	0.36
0.3	0.11	1.15	0.6	0.85	0.3	-0.53	0.06

a n=1

1,3,5-Trimethylbenzene Desorption Data

Cs (ug/L) avg	std	Cw (ug/L) avg	std	amount sorbed (ug/L)	amount sorbed (ng/g)	log amount sorbed	log solution concentration
198	32.7	459.7	28.31	261.7	90.3	1.96	2.66
12	3.38	45.97	a	33.97	11.7	1.07	1.66
2.2	0.36	9	2.11	6.8	2.3	0.37	0.95
143	4.06	326	46	183	63.1	1.80	2.51
64	4.02	175	30	111	38.3	1.58	2.24
14	0.71	44	1	30	10.4	1.01	1.64
2.5	0.08	12	3	9.5	3.3	0.52	1.08
1.6	0.22	4	a	2.4	0.8	-0.08	0.60

a
n=1

Freundlich sorption-desorption isotherm for 1,3,5-Trimethylbenzene at equilibrium.

2-Ethyltoluene Sorption Data

Cs (ug/L) avg	std	Cw (ug/L) avg	std	amount sorbed (ug/L)	amount sorbed (ng/g)	log amount sorbed	log solution concentration
236	21	306	31	70	24.2	1.38	2.49
70	2	143	25	73	25.2	1.40	2.16
22	0	24	1	1	0.7	-0.16	1.38
6	6.4	8	1	2	0.7	-0.16	0.90
3	1	4	0	1	0.3	-0.46	0.60
245.7	3.32	373	23.4	127.3	43.9	1.64	2.57
15.5	2.07	37.3	a	21.8	7.5	0.88	1.57
3.5	0.14	7.7	a	4.2	1.4	0.16	0.89
1.9	0.5	3.7	a	1.8	0.6	-0.21	0.57
0.97	0.14	1.5	a	0.53	0.2	-0.74	0.18
0.52	0.21	0.74	a	0.22	0.1	-1.12	-0.13

a
n=1

2-Ethyltoluene Desorption Data

Cs (ug/L) avg	Cw (ug/L) std	Cw (ug/L) avg	std	amount sorbed (ug/L)	amount sorbed (ng/g)	log amount sorbed	log solution concentration
131	4.22	306	31	175	60.4	1.78	2.49
64	20.4	143	25	79	27.3	1.44	2.16
12	0.72	24	1	12	4.1	0.62	1.38
2	0.06	8	1	6	2.1	0.32	0.90
2	0.59	4	0	2	0.7	-0.16	0.60
11	a	37.3	a	26.3	9.1	0.96	1.57
2.4	a	7.7	a	5.3	1.8	0.26	0.89

a
n=1

Freundlich sorption-desorption isotherm for 2-Ethyltoluene at equilibrium.

1,2,4-Trimethylbenzene Sorption Data

Cs (ug/L) avg	std	Cw (ug/L) avg	std	amount sorbed (ug/L)	amount sorbed (ng/g)	log amount sorbed	log solution concentration
685	70	1072	140	387	133.5	2.13	3.03
245	7	531	62	286	98.7	1.99	2.73
64	4	107	0	43	14.8	1.17	2.03
8	9	13	6	5	1.7	0.24	1.11
962.2	28.4	1565.2	93.24	603	208.0	2.32	3.19
57.9	57.9	156.5	a	98.6	34.0	1.53	2.19
10.8	0.14	31.4	a	20.6	7.1	0.85	1.50
4.9	0.5	15.7	a	10.8	3.7	0.57	1.20
2.4	0.35	6.26	a	3.86	1.3	0.12	0.80
1.3	0.28	3.13	a	1.83	0.6	-0.20	0.50

a
n=1

1,2,4-Trimethylbenzene Desorption Data

Cs (ug/L) avg	std	Cw (ug/L) avg	std	amount sorbed (ug/L)	amount sorbed (ng/g)	log amount sorbed	log solution concentration
479	14.27	1072	140	593	204.6	2.31	3.03
203	17.5	531	62	328	113.2	2.05	2.73
43	3.78	107	0	64	22.1	1.34	2.03
8	0.79	13	6	5	1.7	0.24	1.11
637	86.56	1565.2	a	928.2	320.2	2.51	3.19
24	22.12	156.5	a	132.5	45.7	1.66	2.19
5	4.91	31.4	a	26.4	9.1	0.96	1.50
3.8	0.25	15.7	a	11.9	4.1	0.61	1.20

a
n=1
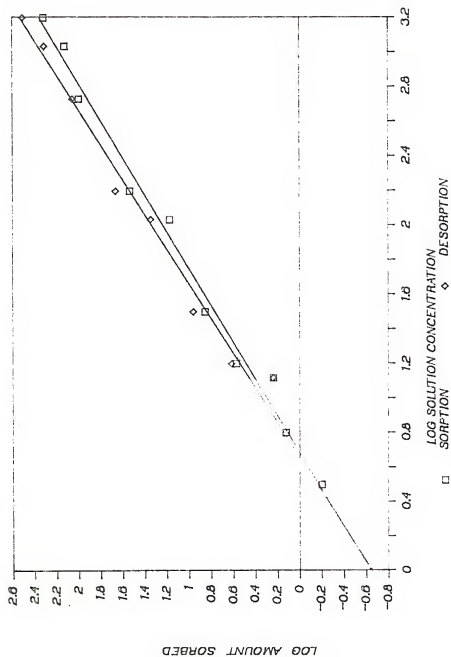
Freundlich sorption-desorption isotherm for 1,2,4-Trimethylbenzene at equilibrium.

210

1,2,3-Trimethylbenzene Sorption Data

Cs (ug/L) avg		Cw (ug/L)			amount sorbed (ug/L)	amount sorbed (ng/g)	log amount sorbed	log solution concentration
	std	avg	std					
284	30	429	82		145	50.0	1.70	2.63
115	4	257	44		142	49.0	1.69	2.41
31	1	43	1		12	4.1	0.62	1.63
11	6	15	2		4	1.4	0.14	1.18
361.4	2.4	558	32.1		196.6	67.8	1.83	2.75
23.1	1.17	55.8	a		32.7	11.3	1.05	1.75
4.3	0.07	11.2	a		6.9	2.4	0.38	1.05
1.9	0.14	5.6	a		3.7	1.3	0.11	0.75
0.89	0.17	2.23	a		1.34	0.5	-0.34	0.35
0.45	0.05	1.11	a		0.66	0.2	-0.64	0.05

a
n=1

1,2,3-Trimethylbenzene Desorption Data

Cs (ug/L) avg	std	Cw (ug/L) avg	std	amount sorbed (ug/L)	amount sorbed (ng/g)	log amount sorbed	log solution concentration
252	34.37	558	32.1	306	105.6	2.02	2.75
18	2.36	55.8	a	37.8	13.0	1.12	1.75
3.2	0.63	11.2	a	8	2.8	0.44	1.05
1.5	0.135	5.6	a	4.1	1.4	0.15	0.75
215	4.48	429	82	214	73.8	1.87	2.63
99	5.77	257	44	158	54.5	1.74	2.41
22	0.61	434	1	412	142.1	2.15	2.64
4.2	0.04	15	2	10.8	3.7	0.57	1.18
2.77	0.63	6	0	3.23	1.1	0.05	0.78

a
n=1
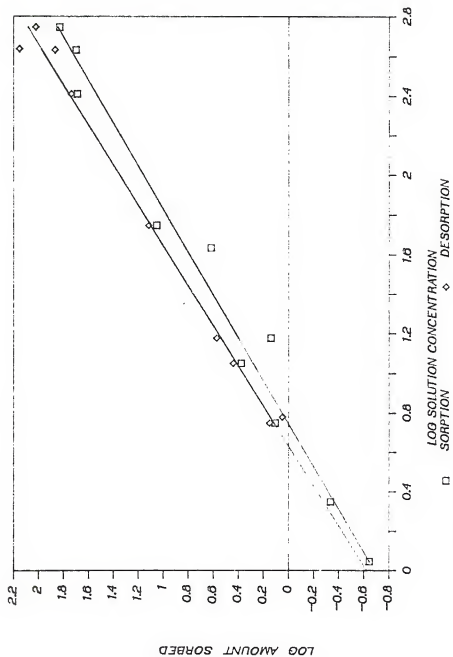
Freundlich sorption-desorption isotherm for 1,2,3-Trimethylbenzene at equilibrium.

APPENDIX D
BREAKTHROUGH CURVE DATA FOR THE SORPTION OF STUDY
COMPOUNDS TO LAKE ALFRED AQUIFER MATERIAL

This appendix presents the breakthrough data for the
aromatic solutes used in this study. The data is presented
as concentrations (ug/L) and as C/C_o (effluent concentration/
influent concentration). Following these data, plots of C/C_o
vs. pore volumes are presented for those compounds not shown
graphically in the body of the dissertation. The final page
of this appendix presents the data for the single solute
breakthrough of benzene.

```
Column Sorption Data
L = 5 cm
v = 0.204 cm/min
pv = 6.9 mL
```

                                Values are as ug/L

mL	BNZ	TOL	ETHBZ	m,p-XYL	o-XYL
1.76	3	4	2	2	2
3.74	2	3	1	2	2
4.71	48	15	3	4	7
5.71	480	158	42	37	83
6.7	1332	514	197	174	335
7.7	2040	825	413	313	598
8.7	2777	1200	677	525	922
9.69	2948	1345	831	655	1115
10.69	3341	1511	951	756	1249
12.69	3877	1826	1238	994	1553
13.69	4081	1935	1343	1070	1658
14.69	4037	1954	1380	1116	1696
15.69	4332	2124	1482	1188	1831
16.69	4420	2165	1551	1246	1905
17.69	4589	2189	1641	1315	2013
18.69	4930	2462	1793	1431	2171
19.69	4531	2368	1801	1472	2183
20.69	4727	2468	1889	1528	2266
21.69	4871	2505	1883	1534	2267
22.69	4523	2415	1904	1537	2301
23.69	4615	2377	1802	1460	2210
24.69	4851	2621	2104	1713	2499
26.69	5454	2985	2385	1952	2905
27.69	5177	2794	2192	1802	2696
28.69	5563	2999	2386	1947	2897
30.7	5345	2838	2213	1822	2759
31.7	5197	2776	2168	1776	2666

```
Column Sorption Data
L = 5 cm
v = 0.204 cm/min
pv = 6.9 mL
```

Values are as ug/L

ispBZ	npBZ	3,4 ET	135 TMB	2 ET	124TMB	123TMB
2	1	4	0	2	2	2
1	1	3	0	2	1	3
2	2	4	1	5	1	2
5	2	7	2	9	4	12
34	7	38	11	47	23	72
90	22	101	33	113	61	168
189	53	225	72	218	127	309
271	85	359	112	314	188	431
337	117	462	145	380	236	511
509	198	695	229	542	357	721
571	226	784	257	594	395	767
616	254	838	282	637	431	821
661	276	926	306	695	461	893
706	302	990	331	730	499	941
767	337	1109	368	799	555	1030
845	370	1164	398	854	589	1085
876	404	1281	431	894	636	1136
922	420	1291	442	917	646	1152
925	423	1306	448	932	654	1179
937	439	1404	461	960	683	1224
883	406	1270	435	909	642	1173
1072	511	1561	532	1079	773	1350
1229	579	1774	617	1270	907	1618
1127	523	1586	562	1156	822	1478
1233	581	1743	617	1258	897	1596
1125	534	1662	580	1196	859	1552
1121	539	1639	579	1178	845	1513

Column Sorption Data as C/Co

PV	BNZ	TOL	Ethyl Bz	m,p-XYL	o-XYL
0.253	0.001	0.002	0.001	0.001	0.001
0.537	0.001	0.001	0.001	0.001	0.001
0.677	0.010	0.006	0.002	0.002	0.003
0.820	0.101	0.062	0.023	0.021	0.037
0.963	0.280	0.201	0.108	0.101	0.150
1.106	0.429	0.322	0.226	0.181	0.269
1.250	0.584	0.469	0.370	0.305	0.414
1.392	0.620	0.525	0.455	0.380	0.500
1.536	0.703	0.590	0.520	0.439	0.560
1.823	0.816	0.713	0.677	0.577	0.697
1.967	0.859	0.756	0.735	0.621	0.744
2.111	0.849	0.763	0.755	0.648	0.761
2.254	0.912	0.830	0.810	0.690	0.822
2.398	0.930	0.846	0.848	0.723	0.855
2.542	0.966	0.855	0.897	0.763	0.903
2.685	1.037	0.962	0.980	0.830	0.974
2.829	0.953	0.925	0.985	0.854	0.980
2.973	0.995	0.964	1.033	0.887	1.017
3.116	1.025	0.979	1.030	0.890	1.018
3.260	0.952	0.944	1.041	0.892	1.033
3.404	0.971	0.929	0.985	0.848	0.992
3.547	1.021	1.024	1.150	0.994	1.122
3.835	1.148	1.166	1.304	1.133	1.304
3.978	1.089	1.091	1.198	1.046	1.210
4.122	1.171	1.171	1.305	1.130	1.300
4.411	1.125	1.109	1.210	1.057	1.238
4.555	1.094	1.084	1.185	1.031	1.197

Column Sorption Data as C/Co

ispBZ	npBZ	3,4 ET	135 TMB	2 ET	124 TMB	123 TMB
0.002	0.002	0.002	0.000	0.002	0.002	0.001
0.001	0.002	0.002	0.000	0.002	0.001	0.003
0.001	0.003	0.002	0.002	0.005	0.002	0.002
0.005	0.003	0.004	0.003	0.009	0.005	0.010
0.034	0.013	0.023	0.021	0.047	0.029	0.059
0.089	0.038	0.062	0.061	0.114	0.079	0.137
0.188	0.094	0.138	0.135	0.219	0.166	0.253
0.269	0.151	0.220	0.211	0.316	0.245	0.352
0.335	0.207	0.283	0.273	0.382	0.308	0.418
0.506	0.350	0.426	0.431	0.545	0.466	0.590
0.568	0.402	0.481	0.483	0.598	0.516	0.627
0.612	0.450	0.514	0.531	0.641	0.563	0.671
0.657	0.490	0.568	0.575	0.699	0.602	0.730
0.702	0.535	0.607	0.623	0.734	0.651	0.769
0.762	0.597	0.681	0.691	0.804	0.725	0.842
0.840	0.656	0.714	0.747	0.859	0.769	0.887
0.871	0.717	0.786	0.810	0.899	0.830	0.929
0.916	0.744	0.792	0.831	0.923	0.843	0.942
0.919	0.749	0.801	0.841	0.938	0.854	0.964
0.932	0.777	0.861	0.867	0.966	0.892	1.001
0.878	0.720	0.779	0.817	0.914	0.838	0.959
1.065	0.906	0.958	1.000	1.086	1.009	1.104
1.222	1.027	1.088	1.160	1.278	1.184	1.323
1.120	0.927	0.973	1.056	1.163	1.073	1.209
1.226	1.030	1.069	1.160	1.266	1.171	1.305
1.118	0.947	1.020	1.090	1.203	1.121	1.269
1.114	0.956	1.006	1.088	1.185	1.103	1.237

Figure showing C/Co versus Pore Volumes, with data series for + 3,4-ETHYLTOLUENE and □ CHLORIDE

C / Co

PORE VOLUMES

□ CHLORIDE   + 2-ETHYLTOLUENE

C/Co

PORE VOLUMES
+ 123TRIMETHYLBENZENE

□ CHLORIDE

```
Single Solute Breakthrough Data
For Benzene

L = 5.0 cm
Volume = 24.5 cu. cm.
Bulk Density = 1.82 g/cu. cm.
1 PV = 6.96 mL
v = 0.204 cm/min.
```

		Benzene	
mL	PV	(ug/L)	C/Co
1.43	0.205	9	0.009
3.43	0.493	12	0.013
4.43	0.636	25	0.027
5.43	0.780	35	0.038
6.43	0.924	84	0.092
7.43	1.068	250	0.272
8.43	1.211	409	0.446
9.43	1.355	529	0.576
10.43	1.499	656	0.714
11.43	1.642	734	0.800
12.43	1.786	779	0.848
13.43	1.930	784	0.854
14.43	2.073	825	0.899
15.43	2.217	853	0.929
16.43	2.361	820	0.893
17.43	2.504	918	1.000
23.43	3.366	909	0.990
24.43	3.510	917	0.999
25.43	3.654	887	0.966
26.43	3.797	748	0.815
27.43	3.941	578	0.629
28.43	4.085	408	0.445
29.43	4.228	298	0.325
30.43	4.372	240	0.261
31.43	4.516	181	0.197
32.43	4.659	143	0.156
33.43	4.803	113	0.123
35.43	5.091	88	0.095
37.43	5.378	81	0.089
39.43	5.665	63	0.068
49.43	7.102	33	0.036

BATCH BIODEGRADATION DATA

This appendix presents data from batch biodegradation experiments one and two. All hydrocarbon concentration values are in units of ug/L. Zero values indicate that the concentration of hydrocarbons was below 0.5 ug/L. Dissolved oxygem values are in units of mg/L.

Treatment 1A

Day	Benzene	Toluene	m,p-Xyl	o-Xyl	3,4 ET	1,3,5 TMB	2 ET	1,2,4 TMB	1,2,3 TMB	DO mg/L
0	756	2023	4452	2597	858	385	441	1239	521	7.2
	803	2101	4760	2639	914	369	438	1317	557	7.3
	926	2389	5258	3031	975	415	353	1447	604	7.4
avg	828	2171	4823	2755	916	390	410	1335	560	7.3
std	72	157	332	195	48	19	41	86	34	0.1
%var	9	7	7	7	5	5	10	6	6	1.1
3	194	88	2740	2344	499	297	255	708	478	1.4
	22	19	506	961	30	140	81	177	141	1.6
avg	108	53	1623	1652	265	218	168	443	309	1.5
std	86	35	1117	692	235	78	87	266	169	0.1
%var	80	65	69	42	89	36	52	60	55	6.7
7	13	19	182	208	42	48	47	47	59	1.5
	79	54	1106	867	200	150	149	219	225	2.0
	73	45	1487	1151	264	214	199	303	318	
avg	55	39	925	742	168	137	132	190	201	1.8
std	30	15	548	395	93	68	64	106	107	0.3
%var	54	38	59	53	55	50	48	56	54	14.3

Treatment 1A

Day	Benzene	Toluene	m,p-Xyl	o-Xyl	3,4 ET	1,3,5 TMB	2 ET	1,2,4 TMB	1,2,3 TMB	DO mg/L
15	0	14	19	25	17	8	35	12	11	2.7
	0	14	62	72	12	0	32	18	15	2.7
avg	0	14	41	48	15	4	33	15	13	4.6
std	0	0	21	24	2	4	1	3	2	4.5
%var		1	52	49	16	100	4	23	14	3.2
31	0	0	0	0	0	0	0	0	0	4.6
	0	0	0	0	0	0	0	0	0	4.5
	0	0	0	0	0	0	0	0	0	3.2
avg	0	0	0	0	0	0	0	0	0	4.1
std	0	0	0	0	0	0	0	0	0	0.6
%var	0	0	0	0	0	0	0	0	0	15.6

Treatment 1B

Day	Benzene	Toluene	m,p-Xyl	o-Xyl	3,4 ET	1,3,5 TMB	2 ET	1,2,4 TMB	1,2,3 TMB	DO mg/L
0	664	1971	3962	2369	701	289	253	1447	604	8.8
	623	1605	3266	1934	623	261	232	1027	468	9.1
	615	1631	3417	2030	653	258	239	892	408	9.2
avg	634	1735	3548	2111	659	269	241	1122	493	9.0
std	22	167	299	187	32	14	9	237	82	0.2
%var	3	10	8	9	5	5	4	21	17	1.9
3	881	1959	2951	2202	601	269	239	692	402	1.5
	567	1219	1310	1274	309	143	136	296	229	
	559	866	565	1668	129	202	188	177	290	1.5
avg	669	1348	1609	1715	346	205	188	388	307	1.5
std	150	456	997	381	194	51	42	220	72	0.0
%var	22	34	62	22	56	25	22	57	23	0.0
7	723	1613	2281	2134	473	228	205	469	365	2.6
	639	1219	1373	2087	347	219	226	260	358	1.6
avg	681	1416	1827	2111	410	224	216	365	362	2.1
std	42	197	454	23	63	4	11	105	3	0.5
%var	6	14	25	1	15	2	5	29	1	23.8

Treatment 1B

Day	Benzene	Toluene	m,p-Xyl	o-Xyl	3,4 ET	1,3,5 TMB	2 ET	1,2,4 TMB	1,2,3 TMB	DO mg/L
15	64	177	230	299	58	14	59	39	73	2.4
	382	652	1642	1414	308	154	142	324	266	2.3
avg	223	415	936	856	183	84	101	181	170	2.4
std	159	237	706	557	125	70	42	143	96	0.0
%var	71	57	75	65	68	84	41	79	57	2.1
31	0	0	8	6	3	3	9	4	17	2.0
	0	0	0	0	0	0	0	0	0	2.9
avg	0	0	8	4	5	3	11	2	10	2.4
std	0	0	7	3	5	3	10	2	7	0.4
%var	0	0	82	73	96	88	89	82	74	15.6

Treatment 1C

Day	Benzene	Toluene	m,p-Xyl	o-Xyl	3,4 ET	1,3,5 TMB	2 ET	1,2,4 TMB	1,2,3 TMB	DO mg/L
0	664	1971	3962	2369	701	289	253	1447	604	10.4
	623	1605	3266	1934	623	261	232	1027	468	
	615	1631	3417	2030	653	258	239	892	408	
avg	634	1735	3548	2111	659	269	241	1122	493	
std	22	167	299	187	32	14	9	237	82	
%var	3	10	8	9	5	5	4	21	17	
3	339	853	1595	983	243	102	96	361	145	3.2
	790	2003	3815	2385	609	262	236	903	403	3.0
	398	355	60	1843	108	203	204	5	325	2.9
avg	509	1070	1823	1737	320	189	179	423	291	3.0
std	200	690	1542	577	212	66	60	369	108	0.1
%var	39	64	85	33	66	35	33	87	37	4.1
7	0	8	4	142	8	25	45	2	78	2.5
	466	397	62	1567	82	168	190	9	319	3.0
	51	52	8	853	23	200	194	5	414	2.4
avg	336	314	140	1213	72	121	155	14	273	
avg	213	193	53	944	46	128	146	8	271	2.6
std	194	166	55	527	31	66	60	4	123	0.3
%var	61	58	77	24	44	20	10	39	17	10.0

234

Treatment 1C

Day	Benzene	Toluene	m,p-Xyl	o-Xyl	3,4 ET	1,3,5 TMB	2 ET	1,2,4 TMB	1,2,3 TMB	DO mg/L
15	14	35	75	252	12	100	51	11	177	3.2
	4	30	53	34	16	7	14	10	15	4.0
	9	42	44	86	19	9	37	9	28	4.1
avg	9	36	57	124	16	39	34	10	73	3.8
std	4	5	13	93	3	43	15	1	74	0.4
%var	48	14	22	75	19	113	45	8	101	10.7
31	0	0	0	0	0	0	5	1	1	2.6
	0	0	0	1	0	35	2	1	17	4.8
avg	0	0	0	0	0	18	4	1	9	3.7
std	0	0	0	0	0	18	2	0	8	1.1
%var	0	0	0	100	0	100	47	6	94	29.7

Treatment 1D

Day	Benzene	Toluene	m,p-Xyl	o-Xyl	3,4 ET	1,3,5 TMB	2 ET	1,2,4 TMB	1,2,3 TMB	DO mg/L
0	706	1816	4137	2370	769	379	318	1103	519	8.8
	1035	2468	5192	3172	948	317	281	1124	469	9.0
avg	871	2142	4665	2771	858	348	300	1114	494	8.9
std	164	326	528	401	90	31	18	10	25	0.1
%var	19	15	11	14	10	9	6	1	5	1.1
3	525	1165	843	1756	255	235	220	133	319	2.9
	727	1376	946	1899	365	214	229	130	350	1.7
	514	734	168	1579	130	194	188	7	277	2.2
avg	589	1092	652	1745	250	214	212	90	315	2.3
std	98	267	345	131	96	16	18	58	30	0.5
%var	17	24	53	8	38	8	8	65	9	21.7
7	326	148	14	1938	75	186	208	4	334	4.3
	223	141	22	1412	45	121	150	6	233	6.0
avg	274	144	18	1675	60	154	179	5	284	5.2
std	52	3	4	263	15	32	29	1	51	0.8
%var	19	2	23	16	25	21	16	16	18	16.5

Treatment 1D

Day	Benzene	Toluene	m,p-Xyl	o-Xyl	3,4 ET	1,3,5 TMB	2 ET	1,2,4 TMB	1,2,3 TMB	DO mg/L
15	305	368	170	1129	62	109	111	6	216	3.0
	136	229	49	1446	46	154	163	5	171	4.1
	65	76	31	1309	18	134	139	4	271	4.9
avg	168	224	83	1295	42	132	138	5	219	4.0
std	101	119	61	130	18	18	21	0	41	0.8
%var	60	53	74	10	44	14	15	10	19	19.5
31	0	1	3	4	4	96	57	2	163	5.0
	2	0	3	21	6	127	84	2	205	5.2
	3	1	0	7	5	99	45	2	143	5.7
	0	1	1	1	2	77	31	1	112	4.7
avg	1	1	2	8	4	100	54	2	155	5.2
std	1	0	1	8	2	18	19	1	34	0.4
%var	107	71	69	91	40	18	36	43	22	7.1

Treatment 1E

Day	Benzene	Toluene	m,p-Xyl	o-Xyl	3,4 ET	1,3,5 TMB	2 ET	1,2,4 TMB	1,2,3 TMB	[DO] mg/L
0	681	1655	3613	2179	663	285	259	985	444	10.5
	804	1991	4163	2555	791	322	291	1134	491	9.9
	591	1429	1429	1913	572	233	219	821	373	10.2
avg	692	1692	3068	2216	675	280	256	980	436	10.2
std	87	231	1181	263	90	37	29	128	49	0.2
%var	13	14	38	12	13	13	11	13	11	2.4
3	606	1390	2333	1699	402	169	161	488	279	3.0
	744	1619	1514	2056	411	204	193	188	345	1.8
	648	1519	2194	1899	417	183	173	372	294	1.5
avg	666	1509	2014	1885	410	185	176	349	306	2.1
std	58	94	358	146	6	14	13	124	28	0.6
%var	9	6	18	8	2	8	8	35	9	30.9
7	243	159	36	1455	68	145	159	6	255	5.0
	224	99	21	1463	68	136	150	5	242	2.4
	311	195	42	1486	71	123	146	5	232	5.0
avg	259	151	33	1468	69	135	152	5	243	4.1
std	37	40	9	13	1	9	5	0	9	1.2
%var	14	26	27	1	2	7	4	9	4	29.7

Treatment 1E

Day/	Benzene	Toluene	m,p-Xyl	o-Xyl	3,4 ET	1,3,5 TMB	2 ET	1,2,4 TMB	1,2,3 TMB	[DO] mg/L
15	26	30	24	901	22	150	139	8	255	6.1
	245	162	38	1302	30	123	132	8	242	4.1
	9	30	25	986	10	104	122	7	232	6.0
avg	93	74	29	1063	21	126	131	8	243	5.4
std	107	62	6	173	8	19	7	0	9	0.9
%var	115	84	22	16	40	15	5	6	4	17.0
31	2	6	9	263	5	65	41	4	99	5.0
	4	1	2	178	2	48	26	4	66	3.7
	15	4	4	192	3	24	24	2	62	7.7
avg	7	4	5	211	3	46	30	3	76	5.5
std	6	2	3	37	1	17	8	1	17	1.7
%var	82	56	59	18	37	37	25	28	22	30.5

Treatment 1F

Day	Benzene	Toluene	m,p-Xyl	o-Xyl	3,4 ET	1,3,5 TMB	2 ET	1,2,4 TMB	1,2,3 TMB	[DO] mg/L
0	681	1655	3613	2179	663	285	259	985	444	10.5
	804	1991	4163	2555	791	322	291	1134	491	9.9
	591	1429	1429	1913	572	233	219	821	373	10.2
avg	692	1692	3068	2216	675	280	256	980	436	10.2
std	87	231	1181	263	90	37	29	128	49	0.2
%var	13	14	38	12	13	13	11	13	11	2.4
3	521	1123	2707	1549	475	112	169	629	258	9.9
	408	884	1737	1143	261	105	106	387	181	9.8
	500	1154	2491	1594	414	174	160	629	285	10.6
avg	476	1054	2312	1429	383	130	145	548	241	9.8
std	49	121	416	203	90	31	28	114	44	0.7
%var	10	11	18	14	23	24	19	21	18	6.7
7	507	470	48	1453	71	136	163	9	251	2.4
	551	228	9	1360	53	102	134	4	206	3.0
	439	466	63	1349	74	130	146	9	233	3.0
avg	499	388	40	1387	66	123	148	7	230	2.8
std	46	113	23	47	9	15	12	2	18	0.3
%var	9	29	57	3	14	12	8	32	8	10.1

Treatment 1F

Day		Benzene	Toluene	m,p-Xyl	o-Xyl	3,4 ET	1,3,5 TMB	2 ET	1,2,4 TMB	1,2,3 TMB	[DO] mg/L
15		594	274	39	1405	55	110	144	12	216	4.0
		463	176	21	1081	41	76	106	8	148	4.5
		619	246	30	1570	61	125	161	12	221	5.4
		218	68	11	864	34	68	101	4	152	7.8
	avg	474	191	25	1230	48	95	128	9	184	5.4
	std	159	79	10	275	11	24	25	3	34	1.5
	%var	34	42	41	22	23	25	20	37	19	26.9
31		205	75	14	702	8	48	56	3	108	7.2
		1	1	4	298	7	62	68	2	141	5.1
		349	92	9	873	11	58	81	2	143	7.4
	avg	185	56	9	624	9	56	68	2	131	6.6
	std	143	40	4	241	2	6	10	0	16	1.0
	%var	77	71	45	39	20	11	15	20	12	15.8

Treatment 1G

Day	Benzene	Toluene	m,p-Xyl	o-Xyl	3,4 ET	1,3,5 TMB	2 ET	1,2,4 TMB	1,2,3 TMB	[DO] mg/L
0	565	1484	3375	2013	612	270	249	881	409	9.0
	615	1339	3158	2237	694	303	271	1066	469	8.6
	654	1443	4053	2463	847	389	336	1192	560	8.3
avg	611	1422	3529	2238	718	321	285	1046	479	8.6
std	36	61	381	184	97	50	37	128	62	0.3
%var	6	4	11	8	14	16	13	12	13	3.3
3	551	1066	2686	1789	453	215	191	701	346	8.0
	118	258	545	371	125	53	51	184	93	7.8
	510	1018	2722	1779	483	228	197	728	353	7.8
avg	393	781	1984	1313	354	165	146	538	264	7.9
std	195	370	1018	666	162	80	67	250	121	0.1
%var	50	47	51	51	46	48	46	47	46	1.2
7	504	992	1623	1590	368	166	152	554	275	8.2
	626	1207	2820	1889	448	206	188	658	341	8.4
	511	1038	2585	1692	427	196	176	643	316	8.0
avg	547	1079	2343	1724	414	189	172	618	311	8.2
std	56	92	518	124	34	17	15	46	27	0.2
%var	10	9	22	7	8	9	9	7	9	2.0

Treatment 1G

Day	Benzene	Toluene	m,p-Xyl	o-Xyl	3,4 ET	1,3,5 TMB	2 ET	1,2,4 TMB	1,2,3 TMB	[DO] mg/L
15	478	934	2036	1326	317	132	120	434	224	7.5
	483	978	2116	1396	339	138	131	440	235	8.4
	432	809	1747	1230	281	118	119	370	207	
avg	464	907	1966	1317	312	129	126	415	222	8.0
std	23	72	158	68	24	8	5	32	12	0.4
%var	5	8	8	5	8	6	4	8	5	5.7
31	528	1028	2278	1538	326	152	143	483	279	7.5
	446	859	1617	1165	217	101	100	317	205	8.0
	180	372	800	610	129	60	60	207	100	7.9
avg	385	753	1565	1104	224	104	101	336	195	7.8
std	149	278	605	381	81	38	34	113	73	0.2
%var	39	37	39	35	36	36	34	34	38	2.8

TREATMENT #2A

treatment #2A

DAY 0	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	1238	7083	227	6498	3185	1443	509	415	1899	689	7.50
	1826	10286	330	9320	4225	2153	769	624	2805	1036	
	1350	7355	226	6903	3353	1576	569	462	2031	765	
	1155	6310	91	6246	3048	1432	527	428	1941	758	
avg	1392	7759	219	7242	3453	1651	594	482	2169	812	7.50
std	260	1509	85	1223	459	295	104	84	370	133	0.00
%variance	19	19	39	17	13	18	17	17	17	16	0

treatment #2A

DAY 2	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4EF	135TMB	2ET	124TMB	123TMB	[DO]
	110	206	22	1273	1340	368	221	198	412	335	3.80
	47	84	31	201	1403	129	257	233	56	97	2.20
	228	302	21	1447	2145	402	305	284	312	473	2.20
avg	128	197	25	974	1629	300	261	238	260	302	2.73
std	75	89	4	551	366	121	34	35	150	155	0.75
%variance	58	45	17	57	22	41	13	15	58	51	27.59

treatment #2A

DAY 6	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	222	602	5	1902	1365	428	200	170	511	303	2.20
	188	395		1605	1033	311	142	123	401	219	2.50
	59	62		739	832	184	124	105	195	209	2.10
avg	156	353	5	1415	1077	308	155	133	369	244	2.27
std	70	222	0	493	220	100	32	27	131	42	0.17
%variance	45	63	0	35	20	32	21	21	35	17	7.50

treatment #2A

DAY 14	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	82	136	9	777	554	159	72	78	148	185	3.10
	195	345		1201	794	241	111	122	181	125	3.70
											3.80
avg	139	241	9	989	674	200	92	100	165	155	3.53
std	56	105	0	212	120	41	20	22	17	30	0.31
%variance	41	43	0	21	18	20	21	22	10	19	8.75

treatment #2A
DAY 21

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	170	148	3	952	522	204	94	77	250	128	2.30
	79	132	1	742	463	174	85	72	170	124	2.20
	186	425		1396	830	331	138	117	345	192	4.00
avg	145	235	2	1030	605	236	106	89	255	148	2.83
std	47	135	1	273	161	68	23	20	72	31	0.83
%variance	32	57	49	26	27	29	22	23	28	21	29.15

Treatment #2A
DAY 34

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	94	104	8	601	355	155	77	66	158	111	2.10
	80	87	9	336	181	94	45	39	93	56	1.90
	45	52	9	325	189	81	40	37	81	60	1.80
avg	73	81	8	421	242	110	54	47	111	76	1.93
std	21	22	1	128	80	32	16	13	34	25	0.12
%variance	28	27	8	30	33	29	30	28	31	33	6.45

TREATMENT #2B

DAY 0	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	1238	7083	227	6498	3185	1443	509	415	1899	689	7.50
	1826	10286	330	9320	4225	2153	769	624	2805	1036	
	1350	7355	226	6903	3353	1576	569	462	2031	765	
	1155	6310	91	6246	3048	1432	527	428	1941	758	
avg	1392	7759	219	7242	3453	1651	594	482	2169	812	7.50
std	260	1509	85	1223	459	295	104	84	370	133	0.00
%variance	19	19	39	17	13	18	17	17	17	16	0.00

Treatment #2B

DAY 2	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	892	4486	84	3434	1964	649	239	221	845	379	2.10
	882	4601	79	3339	1891	591	214	198	716	334	2.50
	732	3739	71	2963	1650	524	193	180	699	297	2.70
avg	835	4275	78	3245	1835	588	215	200	753	337	2.43
std	73	382	5	203	134	51	19	17	65	34	0.25
%variance	9	9	7	6	7	9	9	8	9	10	10.25

Treatment #2B
DAY 7

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	667	2771	55	1857	1245	380	137	135	390	239	2.30
	704	2835	52	1469	1214	323	131	127	250	229	2.10
	592	2419	50	1357	1117	279	108	118	245	200	2.20
avg	654	2675	52	1561	1192	327	125	127	295	223	2.20
std	47	183	2	214	55	41	12	7	67	17	0.08
%variance	7	7	4	14	5	13	10	5	23	7	3.71

Treatment #2B
DAY 15

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	289	887	19	856	916	198	99	107	159	190	3.10
	695	1700	37	469	824	116	102	109	69	175	2.70
avg	492	1294	28	663	870	157	101	108	114	183	2.90
std	203	407	9	194	46	41	2	1	45	8	0.20
%variance	41	31	31	29	5	26	1	1	39	4	6.90

Treatment #2B
DAY 21

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	208	761	17	152	388	58	51	49	13	83	4.40
	498	1585	31	1584	1299	321	145	161	337	293	2.40
	757	1516	37	379	744	112	102	104	51	200	2.70
avg	488	1287	29	705	810	164	99	105	134	192	3.17
std	224	373	8	628	375	113	38	46	145	86	0.88
%variance	46	29	29	89	46	69	39	44	108	45	27.81

Treatment #2B
DAY 34

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	68	142	11	154	118	36	12	18	26	32	3.40
	9	29		8	24	5	2	7	2	10	3.60
	324	353	9	28	165	15	19	24	2	41	3.00
avg	134	175	7	63	102	19	11	16	10	28	3.33
std	137	134	4	65	59	13	7	7	11	13	0.25
%variance	102	77	58	102	57	69	63	43	113	47	7.48

TREATMENT #2C

DAY 0	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	1238	7083	227	6498	3185	1443	509	415	1899	689	7.50
	1826	10286	330	9320	4225	2153	769	624	2805	1036	
	1350	7355	226	6903	3353	1576	569	462	2031	765	
	1155	6310	91	6246	3048	1432	527	428	1941	758	
avg	1392	7759	219	7242	3453	1651	594	482	2169	812	7.50
std	260	1509	85	1223	459	295	104	84	370	133	0.00
%variance	19	19	39	17	13	18	17	17	17	16	0.00

Treatment #2C

DAY 2	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	992	4924	81	3897	2132	716	261	244	963	389	7.00
	913	4703	79	3820	2099	703	265	241	949	395	7.80
	1053	5580	100	4743	2547	894	331	297	1215	483	7.50
avg	986	5069	87	4153	2259	771	286	261	1042	422	7.43
std	57	372	10	418	204	87	32	26	122	43	0.33
%variance	6	7	11	10	9	11	11	10	12	10	4.44

Treatment #2C
DAY 6

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	652	3428	52	2843	1590	533	199	180	712	312	7.40
	740	3812	67	3131	1668	558	203	185	730	308	7.30
	598	3065	45	2473	1409	482	176	163	644	285	7.90
avg	663	3435	55	2816	1556	524	193	176	695	302	7.53
std	59	305	9	269	108	32	12	9	37	12	0.26
%variance	9	9	17	10	7	6	6	5	5	4	3.48

Treatment #2C
DAY 14

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	893	4426	81	3543	1986	617	237	219	868	369	8.10
	849	4222	74	3333	1870	575	217	203	786	341	7.50
	854	4549	81	3339	2147	735	298	254	1040	440	7.80
avg	865	4399	79	3405	2001	642	251	225	898	383	7.80
std	20	135	3	98	114	68	34	21	106	42	0.24
%variance	2	3	4	3	6	11	14	9	12	11	3.14

Treatment #2C
DAY 21

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	712	3677	61	3026	1726	550	214	197	764	353	8.00
	822	4227	69	3448	1969	631	247	227	875	391	7.50
	730	3662	59	2960	1688	546	209	193	764	342	7.70
avg	755	3855	63	3145	1794	576	223	206	801	362	7.73
std	48	263	4	216	124	39	17	15	52	21	0.21
%variance	6	7	7	7	7	7	8	7	7	6	2.66

Treatment #2C
DAY 35

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	922	4052	71	3244	1847	579	226	209	806	348	6.90
	595	2619	41	1828	1087	294	118	111	427	193	7.30
	713	3451	58	2735	1568	491	194	177	686	294	7.60
avg	743	3374	56	2602	1501	455	179	166	640	278	7.27
std	135	588	12	586	314	119	45	41	158	64	0.29
%variance	18	17	22	23	21	26	25	25	25	23	3.95

253

TREATMENT #2D

treatment #2D
day 0

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	1238	7083	227	6498	3185	1443	509	415	1899	689	7.50
	1826	10286	330	9320	4225	2153	769	624	2805	1036	
	1350	7355	226	6903	3353	1576	569	462	2031	765	
	1155	6310	91	6246	3048	1432	527	428	1941	758	
avg	1392	7759	219	7242	3453	1651	594	482	2169	812	7.50
std	260	1509	85	1223	459	295	104	84	370	133	0.00
%variance	19	19	39	17	13	18	17	17	17	16	0.00

treatment #2D
day 2

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	748	3946	191	3479	1937	1026	332	370	1085	550	8.80
	761	4083	76	3660	1909	732	295	246	1016	11	8.80
	743	3871	71	3205	1699	550	205	192	757	315	8.00
avg	751	3967	113	3448	1848	769	277	269	953	292	8.53
std	8	88	56	187	106	196	53	75	141	221	0.38
%variance	1	2	49	5	6	25	19	28	15	76	4.42

treatment #2D
day 7

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	41	73	5	27	654	23	92	143	6	246	4.30
	703	3602	55	2794	1584	478	192	172	656	292	2.20
	735	3724	56	2895	1701	509	196	179	656	309	2.20
avg	493	2466	39	1905	1313	337	160	165	439	282	2.90
std	320	1693	24	1329	468	222	48	16	306	27	0.99
%variance	65	69	61	70	36	66	30	9	70	9	34.14

treatment #2D
day 14

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	73	175	18	73	71	15	14	26	10	21	4.30
	216	1118	11	881	673	174	89	86	187	164	4.10
	137	820		711	504	98	134	80	121	203	2.80
avg	142	704	15	555	416	96	79	64	106	129	3.73
std	59	394	3	348	254	65	49	27	73	78	0.66
%variance	41	56	23	63	61	68	63	42	69	60	17.81

treatment #2D
day 21

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
		19	8	11	11	5	7	12	5	17	4.80
	248	905	16	383	1027	106	129	119	52	256	2.40
	327	691		12	728	27	81	87	2	146	2.60
avg	288	538	12	135	589	46	72	73	20	140	3.27
std	40	377	4	175	426	43	50	45	23	98	1.09
%variance	14	70	34	129	72	94	69	62	116	70	33.28

treatment #2D
day 35

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
		405	5	932	533	170	87	71	213	138	1.60
	108	391	6	41	160	16	7	27	6	35	2.10
	254										
avg	181	398	6	487	347	93	47	49	110	87	1.85
std	73	7	0	446	187	77	40	22	104	52	0.25
%variance	40	2	9	92	54	83	85	45	95	60	13.51

treatment #2E
day 0

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	1238	7083	227	6498	3185	1443	509	415	1899	689	7.50
	1826	10286	330	9320	4225	2153	769	624	2805	1036	
	1350	7355	226	6903	3353	1576	569	462	2031	765	
	1155	6310	91	6246	3048	1432	527	428	1941	758	
avg	1392	7759	219	7242	3453	1651	594	482	2169	812	7.50
std	260	1509	85	1223	459	295	104	84	370	133	0.00
%variance	19	19	39	17	13	18	17	17	17	16	0.00

treatment #2E
day 2

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	607	3060	43	2368	1313	418	149	141	534	229	8.10
	692	3539	45	2717	1502	457	164	155	565	252	8.05
avg	649	3300	44	2543	1408	438	157	148	550	241	8.08
std	43	240	1	174	95	20	8	7	16	12	0.02
%variance	7	7	2	7	7	4	5	5	3	5	0.31

treatment #2E

day 7	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	710	3490	46	2651	1510	426	159	152	573	260	5.10
	613	3031	38	2369	1288	393	143	135	528	227	5.10
	642	3216	41	2493	1390	417	159	149	562	254	3.70
avg	655	3246	42	2504	1396	412	154	145	554	247	4.63
std	41	189	3	115	91	14	8	7	19	14	0.66
%variance	6	6	8	5	6	3	5	5	3	6	14.24

treatment #2E

day 14	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	782	3296	44	2552	1441	423	158	151	592	250	6.00
	760	2918	40	2148	1249	355	132	130	478	224	4.90
	652	3140	22	2238	1290	215	139	131	462	224	5.20
avg	731	3118	35	2313	1327	331	143	137	511	233	5.37
std	57	155	10	173	83	87	11	10	58	12	0.46
%variance	8	5	27	7	6	26	8	7	11	5	8.65

treatment #2E
day 21

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	693	3401	48	2689	1526	448	173	164	634	264	5.00
	1160	5580	78	4406	2455	735	285	261	1012	428	6.10
	801	3881	56	3009	1717	500	195	181	682	304	5.40
avg	885	4287	61	3368	1899	561	218	202	776	332	5.50
std	200	935	13	746	401	125	48	42	168	70	0.45
%variance	23	22	21	22	21	22	22	21	22	21	8.27

treatment #2E
day 35

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	830	3654	51	2489	1397	427	167	144	494	260	3.30
	704	3134	46	2197	1387	343	134	136	468	226	3.90
	732	1123	45	194	1408	116	162	153	76	239	2.60
avg	755	2637	47	1627	1397	295	154	144	346	242	3.27
std	54	1091	3	1020	9	131	15	7	191	14	0.53
%variance	7	41	6	63	1	44	9	5	55	6	16.26

Treatment 2F

treatment #2F

day 0	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	1238	7083	227	6498	3185	1443	509	415	1899	689	7.50
	1826	10286	330	9320	4225	2153	769	624	2805	1036	
	1350	7355	226	6903	3353	1576	569	462	2031	765	
	1155	6310	91	6246	3048	1432	527	428	1941	758	
avg	1392	7759	219	7242	3453	1651	594	482	2169	812	7.50
std	260	1509	85	1223	459	295	104	84	370	133	0.00
%variance	19	19	39	17	13	18	17	17	17	16	0.00

treatment #2F

DAY 2	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	799	3996	38	3568	1929	695	254	239	972	396	9.00
	518	2596	23	2203	1221	403	146	135	539	227	8.10
	640	3415	32	3259	1770	664	252	224	944	253	8.50
avg	652	3336	31	3010	1640	587	217	199	818	292	8.53
std	115	574	6	584	303	131	50	46	198	74	0.37
%variance	18	17	20	19	18	22	23	23	24	25	4.31

Treatment 2E

treatment #2E
day 0

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	1238	7083	227	6498	3185	1443	509	415	1899	689	7.50
	1826	10286	330	9320	4225	2153	769	624	2805	1036	
	1350	7355	226	6903	3353	1576	569	462	2031	765	
	1155	6310	91	6246	3048	1432	527	428	1941	758	
avg	1392	7759	219	7242	3453	1651	594	482	2169	812	7.50
std	260	1509	85	1223	459	295	104	84	370	133	0.00
%variance	19	19	39	17	13	18	17	17	17	16	0.00

treatment #2F
DAY 2

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	799	3996	38	3568	1929	695	254	239	972	396	9.00
	518	2596	23	2203	1221	403	146	135	539	227	8.10
	640	3415	32	3259	1770	664	252	224	944	253	8.50
avg	652	3336	31	3010	1640	587	217	199	818	292	8.53
std	115	574	6	584	303	131	50	46	198	74	0.37
%variance	18	17	20	19	18	22	23	23	24	25	4.31

treatment #2F
DAY 7

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	600	2946	26	2536	1388	457	156	146	600	261	8.00
	687	3294	27	2834	1519	508	186	168	680	290	8.60
	428	2374	19	2000	1133	385	138	127	498	237	8.10
avg	572	2871	24	2457	1347	450	160	147	593	263	8.23
std	108	379	4	345	160	50	20	17	74	22	0.26
%variance	19	13	16	14	12	11	12	11	13	8	3.19

treatment #2F
DAY 14

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	701	3320	30	2651	1502	436	167	160	596	279	7.90
	776	3713	34	2968	1666	498	184	173	663	289	8.10
	730	3578	36	2998	1667	515	196	179	702	302	7.20
avg	736	3537	33	2872	1612	483	182	171	654	290	7.73
std	31	163	2	157	78	34	12	8	44	9	0.39
%variance	4	5	7	5	5	7	7	5	7	3	4.99

treatment #2F
DAY 21

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	542	2770	24	2229	1298	378	146	138	531	246	7.30
	820	4048	40	3374	1928	583	228	221	854	403	7.70
	1309	6405	66	5357	3008	920	349	334	1305	568	7.50
avg	890	4408	43	3653	2078	627	241	231	897	406	7.50
std	317	1506	17	1292	706	223	83	80	317	131	0.16
%variance	36	34	40	35	34	36	35	35	35	32	2.18

treatment #2F
DAY 35

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	659	3131	31	2542	1473	428	166	157	606	266	6.30
	635	3035	27	2497	1449	427	170	157	614	268	7.60
avg	647	3083	29	2520	1461	428	168	157	610	267	6.95
std	12	48	2	22	12	0	2	0	4	1	0.65
%variance	2	2	6	1	1	0	1	0	1	0	9.35

TREATMENT #2G

treatment #2G

day 0	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	237	460		2006	1303	432	181	170	773	333	20.00
	230	397	80	1367	1017	433	161	198	583	363	
	193	386	123	1348	1044	523	181	231	617	396	
avg	220	414	102	1574	1121	463	174	200	658	364	20.00
std	19	33	21	306	129	43	9	25	83	26	0.00
%variance	9	8	21	19	11	9	5	12	13	7	n/a

treatment #2G

day 3	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	0	2	0	1	2	1	47	26	1	33	4.50
	0	2	0	13	69	12	51	46	3	85	4.40
	0	2	0	1	2			3	0	2	
avg	0	2	0	5	24	7	49	25	1	40	4.45
std	0	0	0	6	32	5	2	18	1	34	0.05
%variance	ERR	10	ERR	113	132	79	4	71	106	86	1.12

treatment #2G
day 7

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	0	9	0	3	4	2	0	9	0	5	5.00
	0	4	0	40	105	15	0	18	21	43	2.90
	0	11	0	9	70	5	10	17	3	25	4.40
avg	0	8	0	17	60	7	3	15	8	24	4.10
std	0	3	0	16	42	5	4	4	9	16	0.88
%variance	ERR	37	ERR	94	70	73	141	28	116	65	21.54

treatment #2G
day 14

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	5	60	7	64	61	12	7	18	15	21	3.20
	3	39	8	59	37	12	5	10	13	14	4.00
	0	15	0	57	101	17	14	21	22	33	2.50
	0	4	0	37	83	11	12	26	12	23	
avg	2	29	4	54	70	13	9	19	15	23	3.23
std	2	21	4	10	24	2	3	6	4	7	0.61
%variance	107	73	101	19	34	18	37	30	25	30	18.95

treatment #2G
day 21

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	0	1	0	39	106	14	21	19	18	44	2.90
	0	1	0	4	25	1	10	5	3	2	2.60
	0	3	0	5	48	3	9	10	2	24	3.90
avg	0	2	0	16	60	6	13	11	8	23	3.13
std	0	1	0	16	34	6	5	6	7	17	0.56
%variance	ERR	54	ERR	102	57	95	40	52	92	74	17.74

treatment #2G
day 35

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	2	7	0	4	26	3	5	12	3	16	3.20
	5	30	0	12	12	2	1	4	3	1	3.60
	1	4	0	1	3	0	0	13	0	0	3.60
avg	3	14	0	6	14	2	2	9	2	6	3.47
std	2	12	0	5	10	1	2	4	1	7	0.19
%variance	80	88	ERR	79	70	73	109	43	71	129	5.44

TREATMENT #2H

treatment #2H
day 0

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	237	460		2006	1303	432	181	170	773	333	20.00
	230	397	80	1367	1017	433	161	198	583	363	
	193	386	123	1348	1044	523	181	231	617	396	
avg	220	414	102	1574	1121	463	174	200	658	364	20.00
std	19	33	21	306	129	43	9	25	83	26	0.00
%variance	9	8	21	19	11	9	5	12	13	7	n/a

treatment #2H
day 2

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	136	56	0	0	628	23	55	66	1	152	4.20
	181	164	0	184	809	72	92	95	41	218	8.00
	193	181	0	151	826	69	92	94	26	217	7.00
avg	170	134	0	113	754	55	80	85	23	196	6.40
std	25	55	0	78	90	22	17	13	16	31	1.61
%variance	14	41	ERR	69	12	41	22	16	73	16	25.13

treatment #2H

day 7	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	101	54	0	12	225	8	19	33	5	64	5.00
	25	21	0	6	43	0	6	20	0	21	5.20
	105	74	3	5	164	9	13	33	0	53	5.00
avg	77	50	1	8	144	6	13	29	2	46	5.07
std	37	22	1	3	76	4	5	6	2	18	0.09
%variance	48	44	141	40	53	71	41	21	141	40	1.86

treatment #2H

day 14	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	24	29	0	23	59	5	7	15	7	36	
	26	29	2	22	69	6	7	24	4	27	
	14	3	0	1	13	1	5	2	1	27	
	14	3	0	1	24	1	5	3	1	22	
avg	20	16	1	11	41	3	6	11	3	28	ERR
std	6	13	1	11	23	2	1	9	3	5	ERR
%variance	28	81	153	97	57	65	17	83	82	18	ERR

treatment #2H
day 21

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	25	43	1	37	109	9	11	14	9	44	5.50
	44	25	0	19	139	7	14	18	6	55	4.60
avg	35	34	1	28	124	8	13	16	8	50	5.05
std	10	9	1	9	15	1	2	2	2	5	0.45
%variance	28	26	100	32	12	12	12	12	20	11	8.91

treatment #2H
day 35

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	4	5	0	5	14	3	1	5	3	7	3.50
	45	27	2	15	134	9	16	20	5	54	2.40
avg	25	16	1	10	74	6	9	13	4	31	2.95
std	20	11	1	5	60	3	8	8	1	24	0.55
%variance	84	69	100	50	81	50	88	60	25	77	18.64

TREATMENT #21

treatment #21
day 0

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	237	460		2006	1303	432	181	170	773	333	20.00
	230	397	80	1367	1017	433	161	198	583	363	
	193	386	123	1348	1044	523	181	231	617	396	
avg	220	414	102	1574	1121	463	174	200	658	364	20.00
std	19	33	22	306	129	43	9	25	83	26	0.00
%variance	9	8	21	19	11	9	5	12	13	7	n/a

treatment #21
day 2

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	154	250	11	827	661	149	58	68	255	152	9.60
	142	238	9	822	650	139	59	67	259	152	9.60
avg	148	244	10	825	656	144	59	68	257	152	9.60
std	6	6	1	2	5	5	0	0	2	0	0.00
%variance	4	2	10	0	1	3	1	1	1	0	0.00

treatment #21
day 7

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	163	282		825	700	147	58	81	243	159	8.60
	186	376		894	734	141	57	84	265	153	8.60
avg	175	329	ERR	860	717	144	58	83	254	156	8.60
std	12	47	ERR	35	17	3	0	2	11	3	ERR
%variance	7	14	ERR	4	2	2	1	2	4	2	ERR

treatment #21
day 14

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	157	221		743	594	117	51	62	221	132	7.50
	159	223	4	782	615	122	55	64	245	142	7.20
avg	158	222	4	763	605	120	53	63	233	137	7.35
std	1	1	0	20	10	2	2	1	12	5	0.15
%variance	1	0	0	3	2	2	4	2	5	4	2.04

treatment #21
day 21

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	177	236 bdl		786	639	116	53	59	239	139	7.90
	174	223 bdl		727	606	107	51	56	223	136	7.90
avg	176	230	0	757	623	112	52	58	231	138	7.90
std	2	7	0	30	17	5	1	2	8	2	ERR
%variance	1	3	ERR	4	3	4	2	3	3	1	ERR

treatment #21
day 35

	BNZ	TOL	ETH BZ	m,p-XYL	o-XYL	3,4ET	135TMB	2ET	124TMB	123TMB	[DO]
	107	151		514	442	79	36	41	166	104	6.20
	156	214	5	707	577	110	49	57	218	131	5.50
	170	221	5	707	577	110	48	55	213	127	7.20
avg	144	195	5	643	532	100	44	51	199	121	6.30
std	27	31	0	91	64	15	6	7	23	12	0.70
%variance	19	16	0	14	12	15	13	14	12	10	11.07

APPENDIX F
COLUMN BREAKTHROUGH DATA FOR
BIODEGRADATION COLUMNS

Breakthrough data for columns with flow rates of 1 mL/min and 0.9 mL/hr are presented in tabular form. Breakthrough curves for each compound for the 1 mL/min column are presented following the tabular data.

Column Biodegradation Data

values as ug/L

CUMM ML	BNZ	TOL	EBZ	MPX	OX
=========	=====	=====	=====	=====	====
Co = 1711	7034	1061	3848	1931	
0	0	0	0	0	0
3.897	72.2	59.8	36	0	17
5.553	177.4	163.5	50	0	
6.975	316	272		30	33
8.775	433	412		34	49
9.828	437	485	40	64	68
10.8	455	499	43		69
11.7	490	548	54		87
13.05	467	590	43	62	100
14.4	537	731	54	93	33
15.75	491	690	48	92	141
17.1	513	726	52	110	169
18.225	490	751	55	119	177
22.725	385	649	61	133	206
25.425	479	818	85	182	213
28.125	523	853	86	181	205
29.25	658	1092	93	203	249
44.325	599	1085	95	192	246
50.85	661	1009	88	195	259
54.45	644	1033	95	227	276

L = 2.5 cm
v = 0.003 cm/min

Column Biodegradation Data

Values are C/Co

PV	BZ	TOL	EBZ	MPX	OX
========	========	========	========	========	========
0.000	0.000	0.000	0.000	0.000	0.000
0.570	0.042	0.009	0.034	0.000	0.009
0.812	0.104	0.023	0.047	0.000	0.000
1.020	0.185	0.039		0.008	0.017
1.283	0.253	0.059		0.009	0.025
1.437	0.255	0.069	0.038	0.017	0.035
1.579	0.266	0.071	0.041		0.036
1.711	0.286	0.078	0.051		0.045
1.908	0.273	0.084	0.041	0.016	0.052
2.105	0.314	0.104	0.051	0.024	
2.303	0.287	0.098	0.045	0.024	0.073
2.500	0.300	0.103	0.049	0.029	0.088
2.664	0.286	0.107	0.052	0.031	0.092
3.323	0.225	0.092	0.057	0.035	0.107
3.718	0.280	0.116	0.080	0.047	0.110
4.112	0.306	0.121	0.081	0.047	0.106
4.277	0.385	0.155	0.088	0.053	0.129
6.481	0.350	0.154	0.090	0.050	0.127
7.435	0.386	0.143	0.083	0.051	0.134
7.962	0.376	0.147	0.090	0.059	0.143

L = 2.5 cm
v = 0.003 cm/min
pore water velocity =   14.21290 cm/day
bulk density =   1.8 g/ml
particle density =   2.6 g/ml

```
L = 5 cm
v = 0.204 cm/min
1 pore volume = 6.94 ML
```

Values are as ug/L

CUMM ML	BNZ	TOL	EBZ	MPX	o-XYL
========	========	========	========	========	========
	Co = 5000	2862	2449	2092	2805
1.78	0.7	2.9	0.9	2.8	3.4
3.78	0.7	6.4	0.9	2.1	1.9
4.78	0.7	9.2	0.8	2.9	2.5
5.8	54.4	12.9	2.3	2.6	4.9
6.8	465.6	122.3	26	23.4	50.4
7.8	1346.1	398.7	122	106	211
8.8	2231	769	331.6	251	484
9.8	3104	1186	608	473	817
10.8	3472	1373	775	610	1008
11.8	3822	1552	922	728	1170
13.8	4206	1740	1082	874	1338
15.8	4360	1851	1173	951	1428
16.8	4401	1846	1170	961	1445
17.8	4631	1948	1240	1007	1516
18.8	4414	1921	1264	1038	1531
19.8	5027	2093	1313	1071	1593
20.8	4774	2106	1373	1145	1633
21.8	4302	1897	1245	1016	1498
22.8	4577	1968	1266	1036	1515
25.8	4668	2056	1342	1097	1607
26.8	4642	2035	1320	1087	1578
27.8	4385	1889	1205	986	1487
28.8	4632	2011	1307	1067	1569
29.8	4541	2064	1386	1147	1658
30.8	4378	1809	1080	900	1371
31.8	4730	2149	1437	1193	1710
32.8	4579	2065	1383	1134	1636
33.8	4648	2119	1422	1173	1681
34.8	4914	2241	1513	1237	1780

```
Pore water velocity = 0.680 cm/min.
Particle density = 2.6 g/mL.
Bulk density = 1.82 g/mL.
Volumetric water content = 0.30
```

Values are as ug/L

ISPBZ	NPBZ	3,4ET	135TMB	2ET	124TMB	123TMB
Co = 151	850	2318	836	1479	1145	1786
1.9	1.6	10.5	1.4	2.8	2.2	9.1
0	1.1	5.7	0.9	1.9	1.3	5.3
0	0.6	2.7	0.8	4.2	1.5	1.7
6	0.9	7.3	0	1.6	1.4	1.9
3.1	2	8.4	2.2	9.2	2.9	9.3
21.8	5	27	7.9	34	13	44
68	16	81	26	89	45	130
165	44	204	65	194	109	267
260	78	333	107	290	170	386
359	120	462	155	382	231	501
484	193	727	228	497	335	645
557	245	774	273	563	389	712
564	255	799	284	578	409	748
607	276	860	303	612	428	776
635	302	920	324	641	463	805
658	307	943	330	654	467	819
711	353	1048	367	710	521	899
627	306	915	323	631	460	798
638	312	933	326	636	451	800
673	333	977	348	672	491	837
667	334	926	345	668	481	838
592	289	889	313	616	445	793
659	325	1040	340	663	464	845
709	360	1058	373	718	529	896
522	240	789	274	549	349	702
735	364	1111	382	736	539	908
710	355	1057	365	702	567	871
730	368	1106	378	725	532	895
776	393	1144	402	767	559	948

Column Biodegradation Data

PV	C/Co BNZ	C/Co TOL	C/Co EBZ	C/Co MPX	C/Co o-XYL
0.256	0.000	0.001	0.000	0.001	0.001
0.545	0.000	0.002	0.000	0.001	0.001
0.689	0.000	0.003	0.000	0.001	0.001
0.836	0.011	0.005	0.001	0.001	0.002
0.980	0.093	0.043	0.011	0.011	0.018
1.124	0.269	0.139	0.050	0.051	0.075
1.268	0.446	0.269	0.135	0.120	0.173
1.412	0.621	0.414	0.248	0.226	0.291
1.556	0.694	0.480	0.316	0.292	0.359
1.700	0.764	0.542	0.376	0.348	0.417
1.988	0.841	0.608	0.442	0.418	0.477
2.277	0.872	0.647	0.479	0.455	0.509
2.421	0.880	0.645	0.478	0.459	0.515
2.565	0.926	0.681	0.506	0.481	0.540
2.709	0.883	0.671	0.516	0.496	0.546
2.853	1.005	0.731	0.536	0.512	0.568
2.997	0.955	0.736	0.561	0.547	0.582
3.141	0.860	0.663	0.508	0.486	0.534
3.285	0.915	0.688	0.517	0.495	0.540
3.718	0.933	0.718	0.548	0.524	0.573
3.862	0.928	0.711	0.539	0.520	0.563
4.006	0.877	0.660	0.492	0.471	0.530
4.150	0.926	0.703	0.534	0.510	0.559
4.294	0.908	0.721	0.566	0.548	0.591
4.438	0.875	0.632	0.441	0.430	0.489
4.582	0.946	0.751	0.587	0.570	0.610
4.726	0.916	0.722	0.565	0.542	0.583
4.870	0.929	0.740	0.581	0.561	0.599
5.014	0.983	0.783	0.618	0.591	0.635

Column Biodegradation Data

C/Co ISPBZ	C/Co NPBZ	C/Co 3,4ET	C/Co 135TMB	C/Co 2ET	C/Co 124TMB	C/Co 123TMB
0.001	0.002	0.005	0.002	0.002	0.002	0.005
0.000	0.001	0.002	0.001	0.001	0.001	0.003
0.000	0.001	0.001	0.001	0.003	0.001	0.001
0.004	0.001	0.003	0.000	0.001	0.001	0.001
0.002	0.002	0.004	0.003	0.006	0.003	0.005
0.014	0.006	0.012	0.009	0.023	0.011	0.025
0.045	0.019	0.035	0.031	0.060	0.039	0.073
0.109	0.052	0.088	0.078	0.131	0.095	0.149
0.172	0.092	0.144	0.128	0.196	0.148	0.216
0.237	0.141	0.199	0.185	0.258	0.202	0.280
0.320	0.227	0.314	0.273	0.336	0.292	0.361
0.368	0.288	0.334	0.327	0.381	0.340	0.399
0.373	0.300	0.345	0.340	0.391	0.357	0.419
0.401	0.325	0.371	0.363	0.414	0.374	0.434
0.420	0.355	0.397	0.388	0.433	0.404	0.451
0.435	0.361	0.407	0.395	0.442	0.408	0.458
0.470	0.415	0.452	0.439	0.480	0.455	0.503
0.414	0.360	0.395	0.387	0.427	0.402	0.447
0.422	0.367	0.402	0.390	0.430	0.394	0.448
0.445	0.392	0.421	0.416	0.454	0.429	0.469
0.441	0.393	0.399	0.413	0.452	0.420	0.469
0.391	0.340	0.383	0.375	0.416	0.389	0.444
0.436	0.382	0.449	0.407	0.448	0.405	0.473
0.469	0.424	0.456	0.446	0.485	0.462	0.502
0.345	0.282	0.340	0.328	0.371	0.305	0.393
0.486	0.428	0.479	0.457	0.498	0.471	0.508
0.469	0.418	0.456	0.437	0.475	0.495	0.488
0.483	0.433	0.477	0.452	0.490	0.465	0.501
0.513	0.463	0.493	0.481	0.519	0.488	0.531
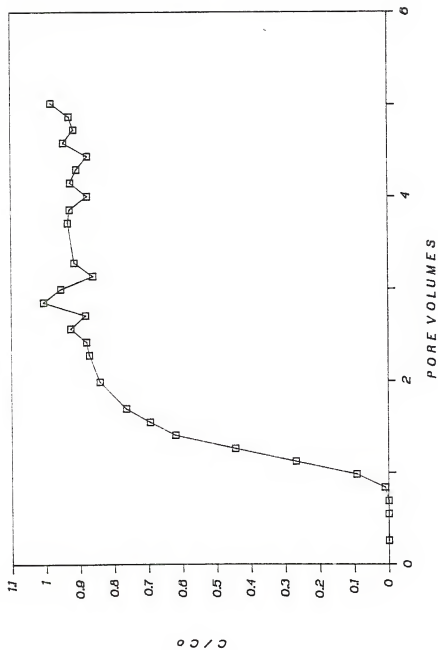
Breakthrough curve for benzene in column biodegradation
experiment performed at a flow rate of 1 mL/min.
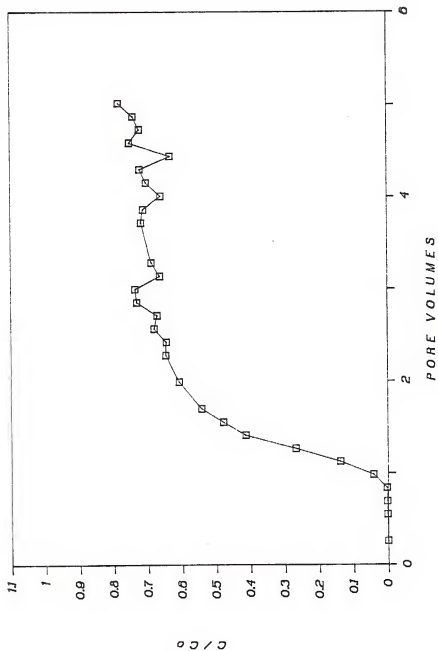
Breakthrough curve for toluene in column biodegradation
experiments performed at a flow rate of 1 mL/min.
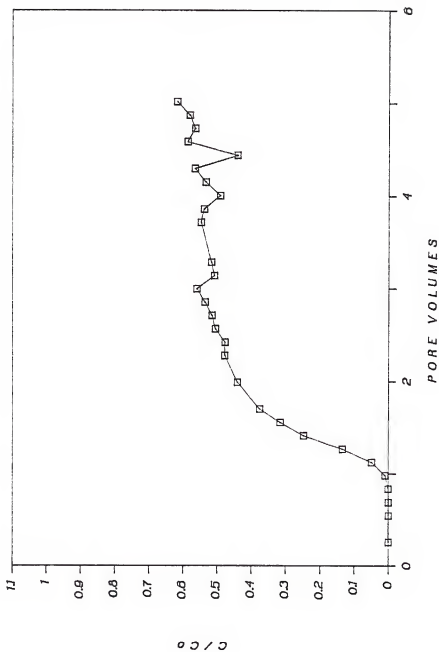
Breakthrough curve for ethylbenzene in column biodegradation experiment performed at a flow rate of 1 mL/mi.
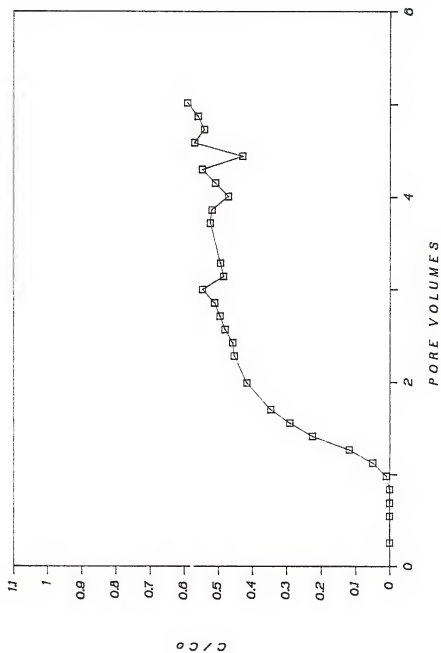
Breakthrough curve for m,p-xylene in column biodegradation
experiment performed at a flow rate of 1 mL/min.
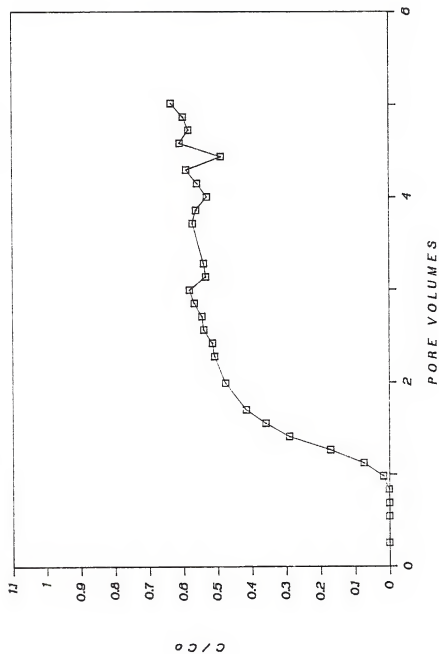
Breakthrough curve for o-xylene in column biodegradation
experiment performed at a flow rate of 1 mL/min.
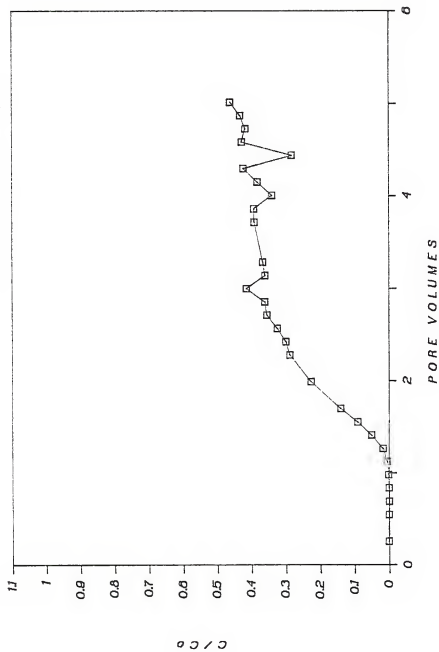
Breakthrough curve for n-propylbenzene in column biodegradation experiment performed at a flow rate of 1 mL/min.
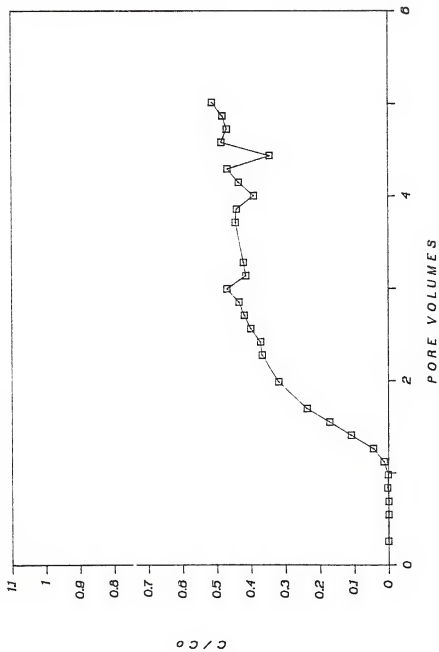
Breakthrough curve for n-propylbenzene in column biodegradation
experiment performed at a flow rate of 1 mL/min.
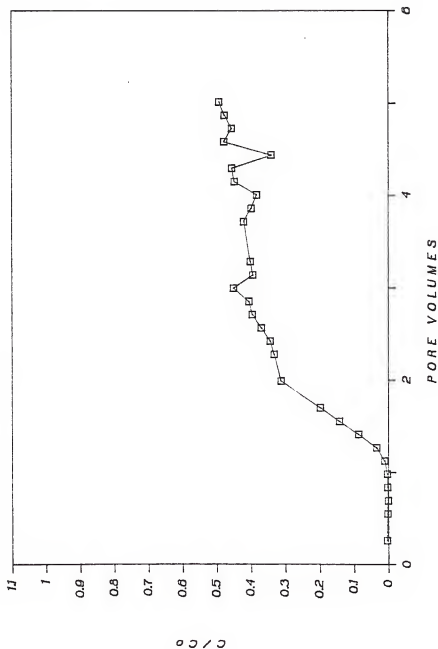
Breakthrough curve for 3 and 4 ethyltoluene in column
biodegradation experiment performed at a flow rate of 1 mL/min.

286
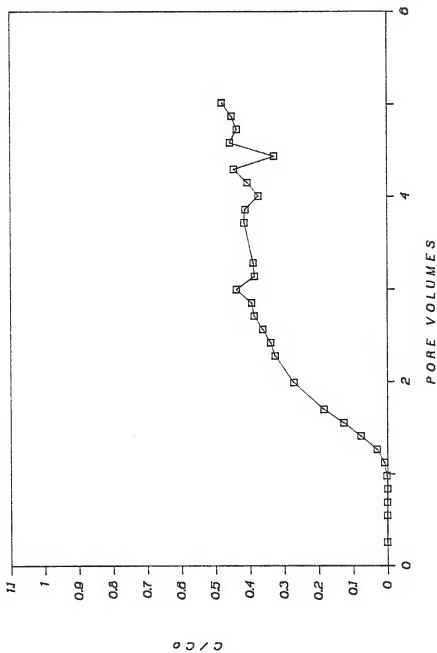
Breakthrough curve for 1,3,5-trimethylbenzene in column
biodegradation experiment performed at a flow rate of 1 mL/min.
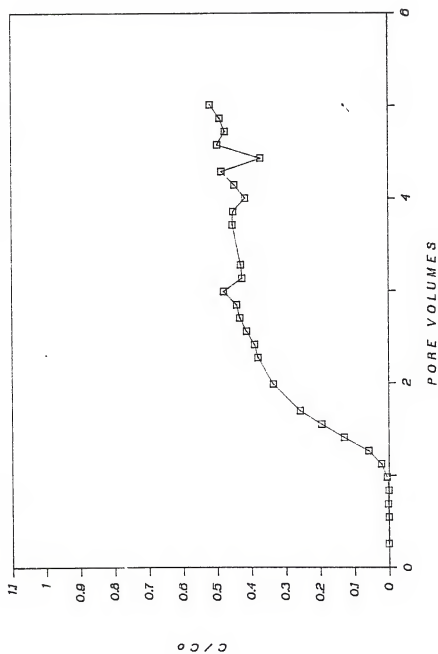
Breakthrough curve for 2-ethyltoluene in column biodegradation
experiment performed at a flow rate of 1 mL/min.
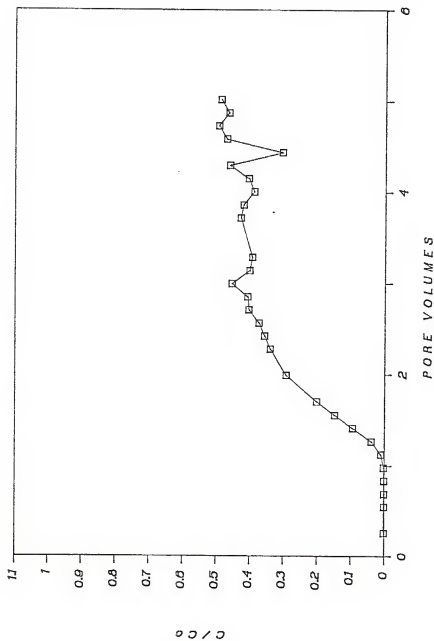
Breakthrough curve for 1,2,4-trimethylbenzene in column biodegradation experiment performed at a flow rate of 1 mL/min.
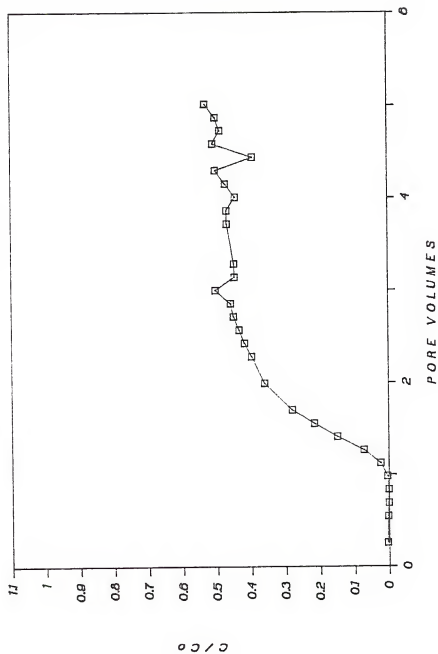
Breakthrough curve for 1,2,3-trimethylbenzene in column biodegradation experiment performed at a flow rate of 1 mL/min.

APPENDIX G
HYDROCARBON CONCENTRATIONS IN MONITORING WELLS AT
THE LAKE ALFRED CITRUS RESEARCH AND EDUCATION CENTER

All concentration values are in units of ug/L. Blank
spaces within the body of each table indicate that the
concentration was below the limit of detection (o.5 ug/L)
of the analytical system. Figure 4-1 shows the location
of each well.

WELL OHM-1

DATE	DAYS	BENZENE	TOLUENE	ETHBEZ	M,P-XYL	O-XYL	isoPBZ	n-PBZ	3,4ET	135TMB	2ET	124TMB	123TMB
02-01-86	0	3318	77110	2929	11841	4681			3699	970	852	4433	995
02-27-86	26	379	14642	1144	12661	5038			3970	1104	1054	4935	1143
03-07-86	34	305	13514	1353	12963	5196			4029	1173	1084	4758	1094
03-20-86	47	286	13294	921	12215	5313			4236	1330	1143	4580	1123
03-27-86	54	321	9518	265	11061	4986			4551	1478	1202	5063	1399
04-25-86	82		9363	1409	14446	5839			4728	1330	1330	5063	1340
05-23-86	111	214	8259	1404	12423	4998			4262	1448	1099	4610	1179
06-25-83	144	161	9923	2296	9692	4034			3578	911	911	3698	1032
07-18-86	167	224	5201	114	9291	3623			2876		622	3198	541
08-28-86	208	637	4996	1188	7865	3725			2990	1390		3700	
09-19-86	229	307	4921	1393	7126	3346	154	294	2665	1285		3450	154
10-22-86	262	108	4291	2059	7595	3607	62	120	2301	966	890	2835	783
11-23-86	294	179	4231	1271	6419	3435	20	15	2124	663	656	2139	847
12-18-86	311	179	2704	82	10270	4490	20	463	2102	696	615	2556	1211
02-20-87	383	411	3799	1472	8787	4109	343	46	1934	1005	808	2716	736
03-17-87	408	147	2491	715	7494	3548	51	0.1	1686	582	466	2149	
04-29-87	451	0.1	0.2	0.1	0.1	0.2	0.1	0.1	0.2		0.8		
05-23-87	481	118	2129	1420	6865	2934	79	159	1589	551	442	2001	685
06-23-87	506	96	1553	588	5018	2145	37	59	1267	453	356	1564	530

W E L L O H M - 2

COMPOUND	DAYS	BENZENE	TOL	ETHBZ	M,P-XYL	O-XYL	isoPBZ	n-PBZ	3,4ET	135TMB	2ET	124TMB	123TMB
			1.04	0.43	3.36	2.57			5.47	2.97	2.35	7.53	2.96
02-01-86	0												
02-27-86	26												
03-07-86	34		695										
03-20-86	47												
03-27-86	54												
04-25-86	82	424											
05-23-86	111												
06-25-86	144	75	1416	632	839	523			232	224	343	710	465
07-18-86	167	305	100	17	55	18			40	11	5	6	43
08-28-86	208											0	
09-19-86	229		33	22	12				20	20		20	444
10-22-86	262		5	2	3	2		2	2	3	3	6	4
11-23-86	294		1					1		1	1	1	6
12-10-86	311	2	14	5	17	8		1	4	8	3	6	7
01-27-87	359	1	4	1	6	3				3	4	3	3
02-20-87	383									1	1	1	2
03-17-87	408	27	77	50	300	56		24	25	70	29	64	305
04-29-87	451		0.6	0.1	0.1	0.1		1.1	0.1	0.6	0.3	0.6	
05-29-87	481	1	2	0	1	2		1	1	9	1	1	6
06-23-87	506		5	3	18	8	3	13	14	6	4	14	5

W E L L   O H M - 3

DATE	DAYS	BNZ	TOL	ETHBZ	M,P-XYL	O-XYL	ISPEZ	n-PRZ	3,4ET	135TMB	2ET	124TMB	123TMB
02-01-86	0	7060	19055		10280	4395			3176	1147	990	3980	1310
02-27-86	26	706	1643		2023	814			552	243	190	795	197
03-07-86	34	4625	13885		7256	2900			2906	887	788	3212	680
03-20-86	47	6437	42663	237	9394	4080			2650	877	818	3231	758
03-27-86	54	5009	15352		10667	4802			4167	1300	1064	4935	1162
04-25-86	82	1951	1819		3372	1903			1143	542	1005	926	473
06-25-86	144	2473	13381	1651	6765	3124			2345	643	657	2573	630
07-18-86	167	3887	18366	5663	7916	3789			2208	759	2151	2507	690
08-28-86	208	1553	14938	1699	7238	3998			3600			4575	
09-19-86	229	4010	34621	2409	11187	5810	142	482	3320	1755	1395	4460	2196
10-22-86	262	2419	35679	4155	13566	7363	71	286	3025	1829	1156	3686	886
10-25-86	265	1231	14909	1529	5859	3083	77	250	1734	769	748	2215	905
10-28-86	268	2804	24028	2281	8526	4275		248	2213	1150	851	2815	837
11-04-86	275	1294	15491	1988	6580	3467	76	221	1844	956	938	2361	809
11-07-86	278	1316	14691	1813	6239	3566	71	185	1675	1232	936	2177	880
11-19-87	290	747	11600	1540	11809	3007	121	352	1567	495	446	1746	529
11-23-86	294	2004	29434	3469	6618	6154	13	8	2929	781	1185	3103	1482
12-10-86	311	1211	12325	150	6873	3342	58	140	1219	405	399	1537	490
01-27-87	359	559	11561	1557	12903	6194	1305	1169	1297	448	334	1634	559
02-20-87	383	3794	20930	4031	10332	5303	55	65	3580	1601	1361	3177	1444
03-17-87	408	1618	17725	494			57	68	2223	749	574	2421	970
04-29-87	451	3399	36695	1711		6994	67	148	2062	702	580	2691	859
06-23-87	506	381	23151	2504	9968	4637			1403	457	402	1816	584

W E L L   O H M - 4

DATE	DAYS	BENZENE	TOLUENE	ETHBZ	M,P-XYL	O-XYL	isoPBZ	n-PBZ	3,AET	135TMB	2ET	124TMB	123TMB
02-01-86	0	10171	32229	2956	18866	8228			6375	1887	1962	7653	2116
02-27-86	26	3930	15197	1925	15246	6979			5299	1616	1418	6245	1635
03-07-86	34	7835	21200	2288	15561	6928			5496	1793	1675	6107	1675
03-20-86	47	5683	17373	2229	15062	6718			4984	1773	1517	5733	1576
03-27-86	54	10290	18441	2381	14170	6158			5595	2482	2653	7263	2417
04-25-86	82	8323	22376	3124	21098	9106			6836	1754	1694	7664	1990
05-23-86	111	4824	20232	2530	17039	7187			5145	2073	1608	5789	1429
06-25-86	144	3109	15756	2649	13030	5463			5160	1251	1304	5485	1411
07-18-86	167	4087	12807	2703	12400	5262			4247	966	1119	5121	1181
08-28-86	208	8540	25654	2746	11210	5454			4127	2400		5483	2276
09-19-86	229	7945	29956	2703	10644	5262			3315	1735	1278	4585	510
10-22-86	262	986	2887	509	1158	648	131	291	499	1227	1081	960	1201
10-25-86	265	7545	21466	2087	10523	5091	209	476	3019	1734	1455	4019	1512
10-28-86	268	3284	11339	1895	9729	4337	170	370	4006	1336	1102	5110	1164
11-04-86	275	4294	13190	2158	8886	4021	196	538	3085	1471	1411	3491	1581
11-07-86	278	4300	14416	2724	10012	4412	119	215	3434	926	830	4119	1073
11-19-86	290	2729	9669	1313	7349	3166	138	441	2993	894	901	3229	1061
11-23-86	294	2512	10217	2180	7848	3499	138	258	2932	904	777	3037	1110
12-10-86	311	2117	10845	1589	12400	4073	132	284	2819	784	663	3440	1036
01-27-87	359	4472	19193	2943	12400	5433	156	274	2460	1248	894	2858	1334
02-20-87	383	1260	3853	1559	8429	3706	76	81	2974	881	704	3711	1099
03-17-87	408	1500	6160	923	8176	3519	68	55	2432	1181	986	3027	1516
04-29-87	451	6681	46241	2269	18555	9215	54	114	3276	411	336	4150	524
06-23-87	506	1551	16940	1837	7006	3314			1102			1462	

W E L L   P - 5

DATE	DAYS	BENZ	TOL	ethbz	m,p-XYL	o-XYL	isBEZ	n-PEZ	3,4ET	135TMB	ZET	124TMB	123TMB
02-01-86	0		9322	1855	2414	1095			7341	2629	2474	8562	2601
02-27-86	26	591	6753	1883	12360	5301			6215	1596	1685	7033	1900
03-07-86	34	113	6159	1478	14826	6219			7033	1960	2020	7900	2019
03-20-86	47	133	8214	2603	9630	4002			3635	1044	1044	3950	1113
03-27-86	54	282	16505	2497	16645	7041			7427	2141	2003	8234	2279
04-25-86	82		16360	3074	20573	8633			6994	1970	1724	7397	1181
05-23-86	111		19037	4080	19134	8246			5869	1796	1555	6379	1474
06-25-86	144	174	11110	2101	9996	4498			5883	1648	1622	5923	1836
07-18-86	167		5154	1823	12240	4519			6348	1277	1668	7119	1231
08-28-86	208											2580	1889
09-19-86	229	677	1455	1063	3874	1767	176	563	2825	1650	1145	3565	1474
10-22-86	262	39	2695	2904	10256	4994	81	257	3720	1587	1344	4677	791
10-25-86	265	33	1063	1169	4760	2315	162	470	1999	908	733	2510	1307
10-28-86	268	97	2000	2079	7754	3931	161	516	3471	1517	1159	4146	1477
11-04-86	275	84	1668	2000	7553	3589	104	133	3040	1587	1339	4645	1564
11-07-86	278	9	306	626	5092	2866	83	164	3412	1490	1300	4166	824
11-19-86	290	24	822	1013	4544	2152	68	139	2145	998	974	2449	692
11-23-86	294	26	660	767	3602	1762	73	156	2201	687	607	1920	834
12-10-86	311	33	931	1294	6646	2969	171	408	2219	741	592	2568	1277
01-27-87	359	1281	1857	1827	8130	3179	1.36		2935	1066	979	4276	653
02-20-87	383	19	17		2057	1962	5	4	1402	662	416	1595	136
03-17-87	408	4	55	42	1187	541			343	121	86	417	
04-29-87	451		0.2		0.1	0.1				0.1	0.8	0.1	
05-29-87	481	9	14	9	41	23	1	4	36	9	12	25	52
06-23-87	506	10	10	13	228	113	1	3	92	38	35	94	52

W E L L   P - 6

DATE	DAYS	BENZENE	TCL	EIHBENZ	M,P-XYL	O-XYL	isoPBZ	n-PBZ	3,4ET	135TMB	2ET	124TMB	123TMB
02-01-86	0	5	53		39	33			1619	651	594	2283	621
02-27-86	26		22		66	149			232	273	168	494	238
03-07-86	34		35		16	62			221	191	125	452	147
03-20-86	47		438	40	302	196			2902	930	615	3094	608
03-27-86	54		372	44	287	268			2079	701	478	2176	471
04-25-86	82				37	87			918	655	270	1660	206
05-23-86	111		13		32	88			849	645	107	789	45
06-25-86	144	17	485	183	89	79			113	102	27	90	42
07-18-86	167	78	106		61	36			13	31	22	28.5	13
09-19-86	229	14	21	11	21	55		13	28	40	23	35	521
10-22-86	262	1	39	25	32	79	3		36	48	35	89	68
10-25-86	265	1	11	5	2	3							
10-28-86	268	2	23	5	112	1	8	3	50	14	113	29	2
11-04-86	275	1	13	4	119	171		3	46	130	31	64	177
11-07-86	278	1	39	33	700	129	3	6	81	32	58	75	46
11-19-86	290	2	33			246			5	72	11		102
11-23-86	294		26	2	10	51	2	2	1	14	1	2	25
12-10-86	311		4	1						2			
01-27-87	359												
02-20-87	383	19	20	16	29	15	14	16	27	14	25	11	10
03-17-87	408		15		6	7					13		
04-29-87	451		41	33	12	32	38	32	184	17	23	20	21
05-29-87	481	1	33	112	379	223	10	24		83	59	236	88
06-23-87	506	0	5	2		1				1	1		1

W E L L   P – 7

DATE	DAYS	BENZ	TOL	EIHENZ	M,P-XYL	O-XYL	isoPBZ	n-PBZ	3,4ET	135TMB	2ET	124TMB	123TMB
02-01-86	0	99	2183	1719	15783	6139			6708	1655	1497	7457	1665
02-27-86	26	79	3265	1745	15440	6320			6510	1660	1595	7260	1725
03-07-86	34	84	3529	1786	16400	7059			7040	2066	1852	8206	1991
03-20-86	47	128	2623	885	9420	5091			6412	2344	1921	6856	1990
03-27-86	54	143	1731	1088	9601	5130			5319	2020	1793	6019	2177
04-25-86	82		2600	1534	13558	6307			7558	2456	2174	8556	2384
05-23-86	111		3844	1366	13066	6461			7801	2359	2090	9032	2064
06-25-86	144	60	7918	3510	9281	4480			5038	1407	1367	5414	804
07-18-86	167	3197	5572	1181	10616	4304			8165	1697	1996	8417	2163
08-28-86	208		694	5562	2651	1873			3125	1640		3835	
09-19-86	229		601	1066	5058	2995	155	421	4160	1810	165	5435	2326
10-22-86	262		376	1157	6216	3607	119	269	3854	1730	1580	4970	1659
10-25-86	265		533	902	6152	3342	288	685	3993	1548	1423	5120	1758
10-28-86	268	135	783	585	7333	4195	92	85	6901	2920	3135	8561	2898
11-04-86	275	91	551	538	7090	4128	121	379	4463	1912	1787	5436	2156
11-07-86	278	85	1992	1979	7496	3694	96	74	3001	1289	1078	3494	1086
11-19-86	290		233	288	3796	2058	118	189	2773	1285	1202	3307	1210
11-23-86	294		354	631	5448	2903	117		4408	1269	1304	4629	1700
12-10-86	311	22	125	4763		2549	136	2993	824	1126		3346	1315
01-27-87	359	205	405	1047	5977	2920	80	365	3780	1478	1003	4531	1556
02-20-87	383		163	499	2182	1617		129		1117	689	1929	
03-17-87	408	102	314	186	2634	1516	123	139	2805	1204	711	2549	1116
04-29-87	451		1.5	1.5		0.5	6	1.2	0.4	0.6	0.5	0.6	0.2
05-29-87	481		17	10	150	84	0.6	6	98	59	45	84	62
06-23-87	506			4	26	15		1	31	18	16	13.4	25

W E L L R A P - 2

DATE	DAYS	BNZ	TOL	ETHBZ	M,P-XYL	O-XYL	isoPBZ	n-PBZ	3,4ET	135TMB	2ET	124TMB	123TMB
06-25-83	144												
07-18-86	167												
08-28-86	208												
09-19-86	229		8	1	6	4			0.3	0.2	0.1		2
10-22-86	262												
11-23-86	294												
12-10-86	311		2		1	1					1		
01-27-87	359												
02-24-87	383												
03-17-87	408		1		1								
04-29-87	451		0.19		0.1	0.08			0.11		0.73		0.04
05-29-87	481		0.25	0.1	0.45	0.2	0.04	0.04	0.44	0.36	0.4	0.3	0.1
06-23-87	506	0	3	0	1	1			0	0	0	0	0

W E L L   R A P - 4

DATE	DAYS	BNZ	TOL	EtBZ	m,p-XYL	o-XYL	iso-PBZ	n-PBZ	3,4ET	135TMB	2ET	124TMB	123TMB
10-22-86	262		224	313	944	325		117	1167	774	485	952	426
11-23-86	294		34	84	415	187			296	166	379	297	104
12-10-86	311		8	39		13		48		167	147	68	85
02-20-87	383	133	152	100	189	97	107	115	190	106	157	67	163
03-17-87	408		65		231	130				196			
04-29-87	451		0.8	0.2	0.1	0.1	0.1	0.1	0.5		0.8	0.3	0.1
05-29-87	481		0.4		0.7	0.5	0.1			0.3	0.6		
06-23-87	506	2	12	114	515	180	10	27	226	95	69	268	109

W E L L   R A P - 6

DATE	DAYS	BNZ	TOL	EtBZ	m,p-XYL	o-XYL	iso-PBZ	n-PBZ	3,4ET	135TMB	2ET	124TMB	123TMB
10-22-86	262	113	170	242	324	142		15	4	10	3		69
11-23-86	294		5	2	2	4	3			1	5	5	
12-10-86	311												46
01-27-87	359		2			1							
02-20-87	383												
03-17-87	408	3	25		995	255			4	2748			5785
04-29-87	451	0.1	0.3	0.2	0.4	0.2	0.2	0.2	0.8	0.1	0.4	0.2	0.2
05-29-87	481		3	1.5	3	3	0.1	0.3	1.5	0.8	1	1.3	
06-23-87	506	0.1	0	0	0	0	0	0	0	0	0	0	1

W E L L   R A P - 5

DATE	DAYS	BENZENE	TOLUENE	ETHBNZ	m,p-XYL	o-XYL	iso-PBZ	n-PBZ	3,4ET	135TMB	2ET	124TMB	123TMB
10-22-86	262	54	208	213	692	499		54	346	674	231	327	5
10-25-86	265		11	18						38	38		18
10-29-86	268	5	42		26	16				64			
11-04-86	275												
11-07-86	278	3	14	21	73	40	2	5	39	19	15	41	20
11-19-86	290	4	10	21	66	43	2	4	32	18	14	37	21
11-23-86	294	20	30	51	237	128	4	7	132	55	46	122	70
12-10-86	311												
02-20-87	383	6	5	3	5	2	3	3	4	2	2	1	1
03-17-87	408	14	145	174	362	103	46	25	348	146	66	164	183
04-29-87	451	0	1.4	0.3	1.2	0.5	0.4	0.2	0.9	0.3	0.7	0.8	0.2
05-29-87	481	0.2	1.3	4	16	3.4	3.5	0.8	3.5	3	3	9	4.3
06-23-87	506	25	48	80	618	108		6.8	255	113	79	301	130

W E L L   R A P - 7

DATE	DAYS	BNZ	TOL	EthBZ	m,p-XYL	o-XYL	iso-PBZ	n-PBZ	3,4ET	135TMB	2ET	124TMB	123TMB
10-22-86	262	0.3	0.5	0.5	1.3	0.6			0.5			0.6	
11-23-86	294												
12-10-86	311		0.1	0.15						1.4			1
01-27-87	359												1
02-20-87	383									1			
03-17-87	408												1
04-29-87	451		0.2		0.24	0.18	0.1		1.5	0.43	0.5	0.3	9.7
05-29-87	481	0.02	0.16	0.04	0.25	2.1					0	1	0
06-23-87	506		0	0	1	0		0	0	0	0		0

W E L L   U F - 1 E

DATE	DAYS	Bnz	Tol	EthBz	m,p-Xyl	o-Xyl	isoPBz	n-PBz	3,4ET	135TMB	2ET	124TMB	123TMB
02-01-86	0												
02-27-86	26		1		1				1			1	
03-07-86	34		365		525						1	296	
03-20-86	47												
03-27-86	54												
04-25-86	82												
05-23-86	111	1											
06-25-86	144												
07-28-86	167	2			1								
08-28-86	208			1									
09-19-86	229	1	1										
10-22-86	262												
11-23-86	294			1							5		
12-10-86	311									1			
02-20-87	383												1
03-17-87	408												
05-29-87	481	0.2	0.5	1.8	1.4	0.6	0.4	0.7	1.2	4.6	3.4	3.8	1.4
06-23-87	506	1	0	5	3	2	1	1	2	6	7	3	3

WELL UF-2M

DATE	DAYS	Benzene	Toluene	EtBz	m,p-Xyl	o-Xyl	isoPBZ	n-PBZ	3,4ET	135TMB	2ET	124TMB	123TMB
02-01-86	0	6219	14284	691	9942	4753			3589	1387	1330	4567	1485
02-27-86	26	5388	15775	1199	9595	4111			3664	1084	979	4203	1090
03-07-86	34	8107	13061	1437	11205	4697			4426	1409	1202	5093	1399
03-20-86	47	4777	20990	1437	9538	4146			4098	1192	1123	4659	1212
03-27-86	54	4500	12128	1297	9932	4500			3664	1389	1143	4354	1221
04-25-86	82	4735	14895	1879	14266	6245			5365	1622	1073	6357	1668
05-23-86	111	3766	14273	2351	11923	5670			4342	1394	1179	5200	1151
06-25-86	144	4905	26302	5579	9567	4356			4315	992	992	4261	858
07-18-86	167	2696	17064	2410	12591	5300			4117	759	1024	4784	931
08-28-86	208	1736	20822	3171	12705	7067			3380			7135	
09-19-86	229	2304	15877	2106	9913	5453			3585	1915	148	4605	2206
10-22-86	262	1468	13289	3410	13490	7321	164	422	3621	2032	1522	4756	1363
10-25-86	265	1721	14961	2805	13295	7372	65	363	3786	1690	1438	4852	1635
11-04-86	268	2840	12812	1443	9781	5460	111	140	2691	1209	1113	3307	1071
11-07-86	275	2147	14454	2400	11649	6424	163	342	3601	1774	1653	4644	1524
11-19-86	278	2576	13374	2153	10042	5496	97	255	2460	1134	2963	2681	1389
11-23-86	290	2102	16723	2565	10812	5867	127	286	2736	992	1126	3488	1164
12-10-86	294	1795	14801	2105	11072	5499	82	180	3248	835	1041	2936	1231
01-27-87	311	2972	9972	1309	8904	4356	58	83	2378	737	730	2504	1060
02-20-87	359	1632	11290	2096	12586	5979	2004	2006	2040	2590	609	3621	978
03-17-87	383	3163	6636	115	7261	3591	11	4	5280	579	2134	1984	224
04-29-87	408	1164	4756	64	8239	4136	14	11	1530	796	470	2592	756
05-29-87	451	1658	7327	1558	8242	3903	83	188	2023	877	639	2876	1034
06-23-87	481	352	5494	2032	9250	3942	78	162	2271	843	666	2606	1074

WELL UF-3W

DATE	DAYS	Benzene	Toluene	EtBEZ	m,p-XYL	o-XYL	isoPBZ	n-PBZ	3,4ET	135TMB	2ET	124TMB	123TMB
02-01-86	0	10867	418		859	604			789	414	237	759	601
02-27-86	26	8747	663		1719	367			690	309	197	1313	453
03-07-86	34	13297	1212	921	3079	997			947	433	276	1458	483
03-20-86	47	14854	6645	1032	4475				394	230	138	630	341
03-27-86	54	13603	437		1722				276	246	148	1625	582
04-25-86	82	14534	1494	1256	3503	827			697	322	54	1179	483
05-23-86	111	15222	534	759	2785	286			1796	295	456	2252	643
06-25-86	144	4569	20140	5730	4855	2749			460	69	92	955	267
07-18-86	167	10489	2786	342	2895	766							
08-28-86	208	1751											
09-19-86	229	11652		1186	532	396			379	193	975	46	128
10-22-86	262	13630	454	2990	961	180	20		29	25	112	15	20
11-23-86	294	9387	59	1227	266	24			48		87	30	51
12-16-86	311	6679	68	12	279	32	19	18	21		101	18	27
02-20-87	383	10089	168	46	436	26			67		113	30	56
03-17-87	408	13441	228	12	573	128				34	46		
04-29-87	451	4558	73	6	325	749		5					
05-29-87	481	1823	365	330	1208	71	17	23	303	116		274	168
06-23-87	506	5875	124	136	250		11	8	74	25		56	66

REFERENCES

Abdul, A.S., T.C. Gibson, and D.N. Rai. (1986). The Effect of
    Organic Carbon on the Adsorption of Fluorene by Aquifer
    Materials. Hazardous Waste and Hazardous Materials 3(4):
    429-440.

Alexander, M. (1985). Biodegradation of Organic Chemicals.
    Environ. Sci. Technol. 19(2): 106-111.

Anderson, M.P. (1979). Using Models to Simulate the Movement
    of Contaminants through Groundwater Flow Systems. In CRC
    Critical Reviews in Environmental Control. Boca Raton,
    FL: CRC Press, pp. 97-156.

Atlas, R.M. (1982). Enumeration and Estimation of Microbial
    Biomass. In Experimental Microbial Ecology. R.I. Burns
    and H.J. Slater (eds). Boston, MA: Blackwell Scientific
    Co., pp. 84-102.

Bailey, G.W., and J.L. White. (1970). Factors Influencing the
    Adsorption, Desorption, and Movement of Pesticides in
    Soil. Residue Review. 32: 29-92.

Barbash, J., and P.V. Roberts. (1986). Volatile Organic
    Chemical Contamination of Groundwater Resources in the
    U.S. Journal Water Pollution Control Federation 58(5):
    343-348.

Barker, J.F., and G.C. Patrick. (1985). Natural Attenuation of
    Aromatic Hydrocarbons in a Shallow Sand Aquifer. In
    Proceedings of NWWA/API Conference on Petroleum
    Hydrocarbons and Organic Chemicals in Ground Water.
    Houston, TX: National Water Well Assoc., pp. 160-176.

Bear, J. (1979). Hydraulics of Groundwater. New York: McGraw
    Hill Book Co.

Bedient, P.B., R.C. Borden, and D.I. Leib. (1985) Basic
    Concepts for Ground Water Transport Modeling. In Ground
    Water Quality. C.H. Ward, W. Giger, and P.L. McCarty
    (eds): New York: John Wiley & Sons, Inc., pp. 512-530.

Biggar, J.W., and D.R. Nielsen. (1962) Some Comments on
    Molecular Diffusion and Hydrodynamic Dispersion in Porous
    Media. Journal of Geophysical Research 67(9): 3636-3637.

Black, C.A. (1965). Methods of Soil Analysis. Monograph 9.
    Madison, Wisconsin: Amer. Soc. Agron.

Blumer, M., J.M. Hunt, J. Atena, and L. Stein. (1973).
    Interaction between Marine Organisms and Oil Pollution.
    Springfield, VA: National Technical Information Service,
    EPA R3-73-042.

Bossert, I., and R. Bartha. (1984). The Fate of Petroleum in
    Soil Ecosystems. In Petroleum Microbiology. R.M. Atlas
    (ed): New York: Macmillan Pub. Co., pp. 435-473.

Boucher, F.R., and G.F. Lee. (1972). Adsorption of Lindane and
    Dieldrin Pesticides on Unconsolidated Aquifer Sands.
    Environ. Sci. Technol. 6(6): 538-543.

Bouwer, E.J., and P.L. McCarty. (1984). Modeling of Trace
    Organics Biotransformation in the Subsurface. Ground
    Water 22(4): 433-440.

Brenner, H. (1962). The Diffusion Model for Longitudinal
    Mixing in Beds of Finite Length: Numerical Values.
    Chemical Engineering Science 17: 229-243.

Briggs, G.G. (1981). Theoretical and Experimental
    Relationships Between Soil Adsorption and Octanol-Water-
    Partition Coefficients. J. Agric. Food Chem. 29: 1050-
    1059.

Britton, L. (1985). Feasibility Studies on the Use of Hydrogen
    Peroxide to Enhance Microbial Degradation of Gasoline.
    Washington, D.C.: American Petroleum Institute
    Publication No.4389.

Brookman, G.T., M. Flanagan, and J.O. Kebe. (1985). Literature Survey: Hydrocarbon Solubilities and Attenuation Mechanisms. Washington, D.C.: American Petroleum Institute Publication No. 4414.

Brown, H.Z., D.R. Bishop, and C.A. Rowan. (1984). The Role of Skin Absorption as a Route of Exposure for Volatile Organic Compounds (VOCs) in Drinking Water. American Journal of Public Health 74(5): 479-484.

Carringer, R.D., J.B. Weber, and T.J. Monaco. (1975). Adsorption-Desorption of Selected Pesticides by Organic Matter and Montmorillonite. J. Agric. Food Chem. 23(3): 568-572.

Chiou, C.T., L.J. Peters, and V.H. Freed. (1979). A Physical Concept of Soil-Water Equilibria for Nonionic Organic Compounds. Science 206: 831-832.

Chiou, C.T., P.E. Porter, and D.W. Schmedding. (1983). Partition Equilibria of Non-ionic Organic Compounds Between Organic Matter and Water. Environ. Sci. Technol. 17: 227-231.

Coleman, W.E., J.W. Munch, J.P. Streicher, H.P. Ringhand, and F.C. Kopfler. (1984). The Identification and Measurement of Components in Gasoline, Kerosene, and No. 2 Fuel Oil that Partition into the Aqueous Phase after Mixing. Arch. Environ. Contam. Toxicol. 13: 171-178.

CRC Handbook of Chemistry and Physics. (1980). Boca Raton, Fl.: CRC Press, Inc.

Curtis, G.P., P.V. Roberts, and M. Reinhard. (1986). A Natural Gradient Experiment on Solute Transport in a Sand Aquifer IV. Sorption of Organic Solutes and its Influence on Mobility. unpublished.

Dagley, S. (1975). A Biochemical Approach to Some Problems of Environmental Pollution. In Essays in Biochemistry. P.N. Campbell and W.N. Adlridge (eds): New York: Academic Press, p. 81.

Davidson, J.M., P.S.C. Rao, and P. Nkedi-Kizza. (1983).
    Physical Processes Influencing Water and Solute Transport
    in Soils. In Chemical Mobility and Reactivity in Soil
    Systems. Madison, Wisconsin: Soil Science Society of
    America, pp. 35-47.

Delfino, J.J., and C.J. Miles. (1985). Aerobic and Anaerobic
    Degradation of Organic Contaminants in Florida
    Groundwater. Soil & Crop Sci. Soc. Fla. Proc.44: 9-14.

DiToro, D.M., and L.M. Horzempa. (1982). Reversible and
    Resistant Components of PCB Adsorption-Desorption
    Isotherms. Environ. Sci. Technol. 16(9): 594-602.

Dowd, R.M. (1984). Leaking Undergound Storage Tanks. Environ.
    Sci. Technol. 18(10): 27-34.

Dupont (1984). Hydrogen Peroxide Solution Storage and
    Handling. Wilmington, DE: E.I. Dupont de Nemours & Co.,
    pp. E-69997.

Evans, W.C. (1977). Biochemistry of the Bacterial Catabolism
    of Aromatic Compounds in Anaerobic Environments. Nature
    270: 17-22.

Fernald, E.A., and D.J. Patton. (1984). Water Resources Atlas
    of Florida. Tallahassee, FL.: Institute of Science and
    Public Affairs, Florida State University.

Fetter, G.W. (1980). Applied Hydrogeology. Columbus, OH:
    Charles E. Merrill Co.

FLDER (1986). Florida Sites List: Petroleum Contamination
    Incidents. Tallahassee, FL: Dept. of Environmental
    Regulation.

Freeze, R.A., and J.A. Cherry. (1979). Groundwater. Englewood
    Cliffs, NJ: Prentice-Hall, Inc.

Ghiorse, W.C., and D.L. Balkwill. (1983). Enumeration and
    Morphological Characterization of Bacteria Indigenous to
    Subsurface Environments. Dev. Ind. Microb. 24: 213-224.

Ghiorse, W.C., and D.L. Balkwill. (1985). Microbiological Characterization of Subsurface Environments. In Ground Water Quality. C.H. Ward, W. Giger, and P.L. McCarty (eds): New York: John Wiley & Sons, Inc., pp. 387-401.

Gibson, D.T., and W.K. Yeh. (1973). Microbial Degradation of Aromatic Hydrocarbons. In The Microbial Degradation of Oil Pollutants. D.G. Ahearn and S.P. Meyers (eds): Baton Rouge: Louisiana State Univ., pp. 33-38.

Hoag, G.E., and M.C. Marley. (1986). Gasoline Residual Saturation in Unsaturated Uniform Aquifer Materials. Journal of the Environmental Engineering Division, ASCE, 112: 586-604.

Houzim, V. (1978). Alterations of the Petroleum Substance in Rock-Water-Air and Rock-Water Interfaces. In International Symposium on Groundwater Pollution by Oil Hydrocarbons. Prague. Worthington, OH: National Well Water Association.

Jamison, V.W., R.L. Raymond, and J.O. Hudson. (1976). Biodegradation of High-Octane Gasoline. Proceedings of Third International Biodegradation Symposium. J.M. Sharpley, A.M. Kaplan (eds.): London, Great Britian: Applied Science Publishers. pp. 187-196.

Jensen, B., E. Arvin, and A.T. Gundersen. (1985). The Degradation of Aromatic Hydrocarbons with Bacteria from Oil Contaminated Aquifers. In Proceedings of NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water, Houston, TX Worthington, OH: National Water Well Association, pp. 421-435.

Kappeler, T., and K. Wuhrmann. (1978a). Microbial Degradation of the Water-Soluble Fraction of Gas Oil - I. Water Research 12: 327-333.

Kappeler, T.H., and K. Wuhrmann. (1978b). Microbial Degradation of the Water Soluble Fraction of Gas Oil - II. Bioassays with Pure Strains. Water Research 12: 335-342.

Karickhoff, S.W., D.S. Brown, and T.A. Scott. (1979). Sorption of Hydrophobic Pollutants on Natural Sediments. Water Research 13: 241-248.

Kenaga, E.E., and C.A. Goring. (1980). Relationship between Water Solubility, Soil Sorption, Octanol-Water Partitioning and Bioconcentration of Chemicals in Biota. In Aquatic Toxicology. J.G. Eaton, P.R. Parish, and A.C. Hendricks (eds): New York: American Soc. of Testing Materials, pp. 78-115.

Killan, G.A. (1987). Hydrogeologic Characterization of Hydrocarbon Pollutant Transport in a Sandy, Unconfined Aquifer. M.S. Thesis, University of Florida.

Klein, D.A., T.C. Loh, and R.A. Goulding. (1971). A Rapid Procedure to Evaluate the Dehydrogenase Activity of Soils Low in Organic Matter. Soil Bio. Biochem. 3: 385-387.

Kuhn, E.P., P.J. Colberg, J.L. Schnoor, O. Wanner, A.J.B. Zehnder, and R.P. Schwarzenbach. (1985). Microbial Transformations of Substituted Benzenes during Infiltration of River Water to Groundwater: Laboratory Column Studies. Environ. Sci. Technol. 19,10: 981-968.

Lapidus, L., and N.R. Amundson. (1952). Mathematics of Adsorption in Beds. VI. The Effect of Longitudinal Diffusion in Ion Exchange and Chromatographic Columns. J. Phys. Chem. 56: 984-988.

Lee, M.D., and D.H. Ward. (1984). Reclamation of Contaminated Aquifers: Biological Techniques. Proceedings of Hazardous Material Spills Conference April 1984, Nashville, TN. Worthington, OH: National Well Water Association, pp. 98-103.

Leo, A., C. Hansch, and D. Elkins. (1971). Partition Coefficients and Their Uses. Chemical Reviews 71: 525-616.

Levenspiel, O. (1972). Chemical Reaction Engineering. New York: John Wiley and Sons, pp. 41-86.

Litchfield, C. (1986). An Overview of The In Situ Bioreclamation of Ground Water: Principles, Practices and Potential. Newark, DL: E.I. dupont de Nemours and Company.

Litchfield, C., and L. Clark. (1973). Bacterial Activity in Ground Waters Containing Petroleum Products. Washington, D.C.: American Petroleum Institute.

MacKay, D.M., P.V. Roberts, and J.A. Cherry. (1985). Transport of Organic Contaminants in Groundwater. Environ. Sci. Technol. 19(5): 384-392.

McCarty, P.L. (1984). Application of Biological Transformation in Ground Water. Proceedings of Second International Conference on Ground Water Quality Research, March 1984, Tulsa, OK. Worthington, OH: National Well Water Association.

McKee, J.E., F.B. Laverty, and R.M. Hertel. (1972). Gasoline in Groundwater. Journal Water Pollution Control Federation 44: 293-302.

McKenna, E.J., and R.D. Heath (1976). Biodegradation of Polynuclear Aromatic Hydrocarbon Pollutants by Soil and Water Microorganisms. University of Illinois, Champaign-Urbana, Research Report No. 113.

Means, J.C., S.G. Wood, J.J. Hassett, and W.L. Banwart. (1982). Sorption of Amino-and Carboxy-Substituted Aromatic Hydrocarbons by Sediments and Soils. Environ. Sci. Technol. 16: 93-98.

Milgelgrin, U., and Z. Gerstl. (1983). Reevaluation of Partitioning as a Mechanism of Nonionic Chemicals Adsorption in Soils. J. Environ. Qual. 12(1): 1-11.

Miller, C.T., and W.J. Weber. (1984). Modeling Organic Contaminant Partitioning in Ground-Water Systems. Ground Water 22,3: 584-591.

Mitchell, R (1974). Introduction to Environmental Microbiology. Englewood Cliffs, N.J.: Prentice-Hall Inc.

Moore, J.W., and E.A. Moore. (1976). _Environmental Chemistry_. New York: Academic Press.

Nathawani, J.S., and C.R. Phillips. (1977). Absorption-Desorption of Selected Hydrocarbons in Crude Oil on Soils. _Chemosphere_ 6: 157-162.

Nkedi-Kizza, P., P.S.C. Rao, and A.G. Hornsby. (1987). The Influence of Organic Co-Solvents on Leaching of Hydrophobic Organic Chemicals through Soils. _Environ. Sci. Technol._ 21(11): 1107-1111.

Pinder, G.F. (1984). Groundwater Contaminant Transport Modeling. _Environ. Sci. Technol._ 18(4): 108-114.

Rao, P.S.C. (1985). Class Lecture Notes, SOS 6622. University of FLorida, Soil Science Department.

Rao, P.S.C., and J.M. Davidson. (1979). Adsorption and Movement of Selected Pesticides at High Concentrations in Soils. _Water Research_ 13: 375-380.

Rao, P.S.C., and J.M. Davidson. (1980). Estimation of Pesticide Retention and Transformation Parameters Required in Non-Point Source Pollution Models. In _Environmental Impact of Non-Point Source Pollution_. M.R. Overcash and J.M. Davidson (eds): Ann Arbor, MI: Ann Arbor Science Publishing Inc., pp. 23-67.

Rao, P.S.C., J.M. Davidson, R.E. Jessup and H.M. Selim. (1979). Evaluation of Conceptual Models for Describing Non Equilibrium Adsorption-Desorption of Pesticides During Steady Flow in Soils. _Soil Sci. Soc. Am. J._ 43: 904-912.

Rao, P.S.C., A.G. Hornsby, D.P. Kilcrease, and P. Nkedi-Kizza. (1985). Sorption and Transport of Hydrophobic Organic Chemicals in Aqueous and Mixed Solvent Systems: Model Development and Preliminary Evaluation. <u>J. Environ. Qual.</u> 14: 376-382.

Rao, P.S.C., and R.E. Jessup. (1983). Sorption and Movement of Pesticides and Other Toxic Organic Substances in Soils. In <u>Chemical Mobility and Reactivity in Soil Systems.</u> Madison, WI: Soil Science Soc. of America, p. Ch. 13.

Raymond, R.L., V.W. Jamison, and J.O. Hudson. (1975a). <u>Beneficial Stimulation of Bacterial Activity in Groundwaters Containing Petroleum Products.</u> AIChE Symposium Series 73. pp. 390-404.

Raymond, R.L., V.W. Jamison, and J.O. Hudson. (1975b). <u>Final Report on Beneficial Stimulation of Bacterial Activity in Groundwaters Containing Petroleum Products.</u> Washington, D.C.: American Petroleum Institute, API Project OS21.2,

Raymond, R.L., V.W. Jamison, and J.O. Hudson. (1977). <u>Bacterial Growth in and Penetration of Consolidated and Unconsolidated Sands Containing Gasoline.</u> Washington, D.C.: American Petroleum Institute, API Project 307-76.

Roberts, P.V., M. Reinhard, G.D. Hopkins, and R.S. Summers. (1985). Advection-Dispersion-Sorption Models for Simulating the Transport of Organic Contaminants. In <u>Ground Water Quality.</u> C.H. Ward, W. Giger, and P.L. McCarty (eds): New York: John Wiley & Sons, Inc., pp. 425-445.

Rodgers, R.D., J.C. McFarlane, and A.J. Cross. (1980). Adsorption and Desorption of Benzene in Two Soils and Montmorillonite Clay. <u>Environ. Sci. Technol.</u> 14: 457-461.

Sabljic, A. (1984). Predictions of the Nature and Strength of Soil Sorption of Organic Pollutants by Molecular Topology. <u>J. Agric. Food Chem.</u> 32(2): 243-246.

Sabljic, A. (1987). On the Prediction of Soil Sorption
    Coefficients of Organic Pollutants from Molecular
    Structure: Application of Molecular Topology Model.
    Environ. Sci. Technol. 21(4): 358-366.

Sanders, W.N., and J.B. Maynard. (1968). Capillary Gas
    Chromatographic Method for Determining the C3-C
    Hydrocarbons in Full Range Motor Gasolines. Anal. Chem.
    40(3): 67-72.

Schwarzenbach, R.P., W. Giger, E. Hoehn, and J.K. Schneider.
    (1983). Behavior of Organic Compounds During
    Infiltration of River Water to Groundwater, Field
    Studies. Environ. Sci. Technol. 17: 472-479.

Schwarzenbach, R.P., and J. Westall. (1981). Transport of
    Nonpolar Organic Compounds from Surface Water to Ground
    Water. Environ. Sci. Technol. 15: 1360-1367

Shehata, A. (1985). A Multi-Route Exposure Assessment to
    Chemically Contaminated Drinking Water and Health
    Significance with Emphasis on Gasoline. Augusta, ME:
    Maine Dept. of Human Services.

Smith, L., and F.W. Schwartz. (1980). Mass Transport: 1. A
    Stochastic Analysis of Macroscopic Dispersion. Water
    Resour. Res. 16: 303-313.

Spangler, D. (1984). Hydrogeologic Study of University of
    Florida Agricultural Research and Education Center,
    Lake Alfred, Florida. unpublished report.

Standard Methods for the Examination of Water and Wastewater
    15th Edition. (1980). Washington, D.C.: American Public
    Health Assoc.

Swokowski, E.A. (1975). Calculus With Analytical Geometry.
    Boston: Prindle, Weber and Schmidt, p. 209.

Thomas, H.A. (1950). Graphical Determination of BOD Curve
    Constants. Water and Sewage Works 97: 123.

Trevors, J.T. (1982). Effect of Pentachlorophenol on Electron Transport System Activity in Soil. Bull. Environ. Contam. Toxicol. 29: 727-730.

Trevors, J.T., C.I. Mayfield, and W.E. Inniss. (1982). Measurement of Electron Transport System (ETS) Activity in Soil. Microb. Ecology 8: 163-168.

TRI (1982). Enhancing the Microbial Degradation of Underground Gasoline by Increasing the Available Oxygen. Austin, TX.: Texas Research Institute.

USPHS (1981). Second Annual Report on Carcinogens. Research Triangle Park, NC: United States Public Health Service.

Van Genuchten, M.T., and J.C. Parker. (1984). Boundary Conditions for Displacement Experiments through Short Laboratory Soil Columns. Soil Sci. Soc. Am. J. 48: 703-708.

Voice, T.C., and W.J. Weber. (1983). Sorption of Hydrophobic Compounds by Sediments, Soils and Suspended Solids - I: Theory and Background. Water Research 17: 1433-1441.

Waksman, S.A. (1916). Bacterial Numbers in Soil at Different Depths and in Different Seasons of the Year. Soil Science 1: 316-330.

Weber, W.J., T.C. Voice, M. Pirbazari, G.E. Hunt, and D.M. Ulanoff. (1983). Sorption of Hydrophobic Compounds by Sediments, Soils and Suspended Solids II: Sorbent Evaluation Studies. Water Research 17(10): 1443-1452.

Webster, J.J., G.J. Hampton, J.T. Wilson, W.C. Ghiorse, and F.R. Leach. (1985). Determination of Microbial Cell Numbers in Subsurface Samples. Ground Water 23,1: 17-25.

Williams, D.E., and D.G. Wilder. (1971). Gasoline Pollution of a Groundwater Reservoir -- A Case History. In Proceedings of the National Groundwater Quality Symposium. Worthington, OH: National Well Water Association.

Wilson, B.H., and J.F. Rees. (1985). Biotransformation of Gasoline Hydrocarbons in Methanogenic Aquifer Material. In _Proceedings of NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water_, Houston, TX. Worthington, OH: National Water Well Assoc., pp. 128-139.

Wilson, J.T., C.G. Enfield, W.J. Dunlap, R.L. Crosby, D.A. Foster, and L.B. Baskin. (1981). Transport and Fate of Selected Organic Pollutants in a Sandy Soil. _J. Environ. Qual._ 10: 501-506.

Wilson, J.T., L.E. Leach, M. Henson, and J.N. Jones. (1986). In Situ Biorestoration as a Ground Water Remediation Technique. _Ground Water Monitoring Review_ 6(4): 56-64.

Wilson, J.T., and J.F. McNabb. (1983). Biological Transformation of Organic Pollutants in Groundwater. _EOS_ 64(33): 505-508.

Wilson, J.T., J.F. McNabb, D.L. Balkwill, and W.C. Ghiorze. (1983a). Enumeration and Characterization of Bacteria Indigenous to a Shallow Water Table Aquifer. _Ground Water_ 21: 134-142.

Wilson, J.T., J.F McNabb, J.W. Cochran, T.H. Wang, M.B. Tomson, and P.B. Bedient. (1983b). Adaption of Ground-Water Microorganisms at a Creosote Waste Disposal Site. Presented Before the Division of Environmental Chemistry. Washington, D.C.: American Chemical Society.

Wilson, S.B. (1985). In Situ Biosurfactant Production: An Aid to the Biodegradation of Organic Ground Water Contaminants. In _Proceedings of The Petroleum Hydrocarbons and Organic Chemicals in Ground Water - Prevention, Detection and Restoration_, Houston, TX. Worthington, OH: National Water Well Assoc., pp. 436-444.

Windholz, M. (1976). *The Merck Index, 9th Edition*. Rahway, NJ: Merck Co.

Woodburn, K. (1985). Thermodynamics and Mechansims of Sorption for Hydrophobic Organic Compounds on Natural and Artificial Sorbent Materials. Ph.D. Dissertation, University of Florida.
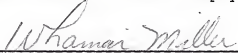
Joseph Timothy Angley was born on November 15, 1958, in Boston, Massachusetts. He prepared for college at Silver Lake Regional High School in Kingston, Massachusetts, and graduated in 1976. He attended Bowdoin College in Brunswick, Maine, where he graduated with a Bachelor of Arts degree in biology, cum laude, in 1980. He was accepted for graduate study at the University of Florida, Department of environmental engineering sciences, in January 1981 and completed the Master of Science degree in 1984 with a study of the mutagenicity of chlorinated sewage effluents. He is currently a candidate for the Doctor of Philosophy degree in Environmental Engineering Sciences.

His related work experience has included employment as a graduate teaching assistant for several water chemistry courses, and as a graduate research associate on several grants and projects.

In 1986 he was one of 22 graduate students nationwide to receive an American Chemical Society Division of Environmental Chemistry Graduate Student Award. He is a member of the American Chemical Society and the Water Pollution Control Federation.

He was married to Elizabeth Euliano in August, 1985 and together they have one child, David, 1 year old.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.
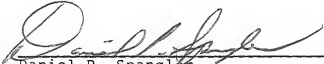
Wesley Lamar Miller, Chairman
Professor of Environmental
    Engineering Sciences

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Joseph J. Delfino, Cochairman
Professor of Environmental
    Engineering Sciences

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Daniel P. Spangler
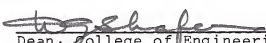Associate Professor
    of Geology

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Paul A. Chadik
Assistant Professor of
Environmental Engineering Sciences

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Peter Nkedi-Kizza
Assistant Professor of
    Soil Science

This dissertation was submitted to the Graduate Faculty of the College of Engineering and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December, 1987

Dean, College of Engineering

Dean, Graduate School